APPLICATION OF AN ARGON-COOLED INDUCTIVELY COUPLED PLASMA TO THE ANALYSIS OF METALS IN LUBRICATING OILS

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Thesis submitted in partial fulfilment of the
Degree of Master of Science
in the
Department of Analytical Science

University of Cape Town

September 1987

ABSTRACT

A sequential atomic emission spectrometer, using a low power (1,7 kW) argon-cooled inductively coupled plasma (ICP) system, was used for the determination of wear metals and additives in lubricating oils with xylene as solvent.

The modified Simplex method was applied to establish the optimum experimental parameters for 21 individual spectral lines. The optimization was applied to single element analysis on the basis of net signal-to-background ratio (SBR) using the standard cross flow nebulizer and then repeated using the high solids Babington-type nebulizer. Weighted compromise conditions were calculated resulting in a maximum loss of 50% in the SBRs of the individual elements. These conditions result in an analytically useful plasma that gives low detection limits and high sensitivities for the analysis of metals in lubricating oils.

Analytical parameters such as detection limit and analytical range for the analysis of 17 elements present in lubricating oil as wear metals or contaminants and 4 other elements present in the most common lubricating oil additives were determined.

The detection limits reported here for oil in xylene are of the same order as the published limits for aqueous and for oil-in-MIBK solutions. However, the most valuable property of the ICP-AES was found to be the astounding analytical range which allows determinations to be made over a large concentration range without the need for serial dilutions.

The effect of sample preparation was investigated by employing ultrasonic agitation prior to withdrawing the used oil from the sample vial. An upward trend was found in the element concentrations from manual shaking of the oil to ultrasonic agitation, indicating a particle distribution effect.

Finally, the technique was tested successfully by analysing an NBS reference standard and by participating in several "round robin" used oil analyses.

ICP-atomic emission spectrometry can be successfully applied to the analysis of metals in lubricating oils with a speed, accuracy and precision which at least equals, and even improves upon any other of the established techniques.

OPSOMMING

'n Sekwensie-atoomemissiespektrometer, toegerus met 'n lae drywing (1,7 kW), argonverkoelde, induktiefgekoppelde plasma (IGP), is gebruik vir die bepaling van slytmetale en bymiddels in smeerolies met xileen as oplosmiddel.

Die Gewysigde Simpleksmetode is gebruik om optimum eksperimenteleparameters vir 21 indiwiduele spektrale lyne te bepaal. Die optimisering is toegepas op enkelelementanalise op die basis van netto sein-tot-agtergrondverhouding (SAV) terwyl die konvensionele kruisvloeiverstuiwer gebruik is en daarna herhaal met 'n Babbington-tipe verstuiwer. Kompromiskondisies is bereken wat aanleiding gegee het tot 'n maksimum verlies van 50% in die SAV's van die indiwiduele elemente. Hierdie kondisies het gelei tot 'n analities nuttige plasma wat lae speurgrense en hoë sensitiwiteite vir die analise van metale in olies gee.

Analitiese parameters soos speurgrens en analitiese gebied vir die analise van 17 elemente wat in olie teenwoordig is as slytmetale of kontaminante en 4 ander elemente wat in die mees algemene smeeroliebymiddels voorkom is bepaal.

Die speurgrense wat hier geraporteer is, is van dieselfde ordegrootte as die gepubliseerde waardes vir waterige en vir olie-in-MIBK oplossings. Die mees waardevolle eienskap van IGP-AES is egter die verbasende lang analitiese gebied wat tot gevolg het dat analises oor 'n groot konsentrasiegebeid gedoen kan word sonder enige veelvuldige verdunnings.

Die effek van monstervoorbereiding is ondersoek deur die monsterhouer in 'n ultrasoniese bad te skud voordat die monster vir analises geneem word. 'n Hoër konsentrasie is waargeneem waneer die monster in 'n ultrasoniese bad geskud word voor aanbieding vir analise wat baie duidelik aandui op 'n partikel-verspreidingseffek.

Die tegniek is suksesvol geëvalueer deur 'n NBS-verwysingstandaard te analiseer en deel te neem aan die analise van verskeie "rondomtalie" gebruikte oliemonsters.

IGP-atoomemissiespektrometrie kan suksesvol aangewend word vir die analise van metale in smeerolies met analisetyd, akkuraatheid en presissie wat ten minste dieselfde of beter is as enige van die gevestigde tegnieke.

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CHAPTER 1: INTRODUCTION

Metals present in lubricating oils are derived from three sources: **additives** (deliberate addition of metals); **contamination** (accidental addition of metals); and **wear** (metals entering the oil from mechanical wearing of moving parts).

Additives are mixed into liquid lubricants to enhance their lubricating properties. Metal containing lubricant additives can be divided into the following groups (Sychra et al., 1981): **antioxidants**; **detergents** and **dispersants**; **corrosion inhibitors**; **load carrying additives**; **antiwear** and extreme **pressure additives**; **emulsifying agents**; and **anti-foam** agents. Any decrease in the concentration of one or more of these additives indicates some degradation of the lubricant with a consequent reduction in lubricant efficiency. The most common metal additives are calcium, magnesium and zinc compounds.

Contaminants arise from dust (Si) and from coolant system leaks (B, Cr and Na).

Wear occurs between moving parts in any mechanical system and can be described as the mechanical or chemical removal of material from one or more of the moving surfaces. Wear is reduced by coating all moving parts with a thin layer of lubricant which not only forms a protective layer, but also

cools the various parts. Under certain conditions, such as during extended usage, the oil layer may be broken for a short period of time seriously aggravating wear. In all circulating oil systems wear products will enter the oil.

Small sized metal particles are formed when wear is minimal but the number and the size of the particles increases as the rate of wear increases.

Any sign of abnormal wear indicates that one or more of the parts is wearing rapidly and that potentially serious problems may arise in the engine. Many investigations of trace metal distribution in engine oils have permitted identification of components which are wearing excessively long before catastrophic failure occurs, and without the extensive task of dismantling the entire engine. Hence preventive maintenance can be performed when required, resulting in considerable cost savings and greatly reduced down-time of expensive machinery. Early prediction of breakdowns can prevent costly repairs or save lives, for example in the aeronautics field.

Wear of a specific component is heralded by either an increase in the concentration of a particular metal, or by the sudden appearance of a metal in the oil. Since different engine components are constructed of different alloys, an increase of a particular metal can be used to identify which specific component is about to fail. An increase of chromium for instance, suggests piston wear, while an increase in lead and copper content indicates wearing of the bearings.

Metals found in engine oil and their possible origins are listed in Table 1 (McKenzie, 1981).

Many Spectrometric Oil Analysis Programmes (SOAP) have been implemented by the South African Air Force (SAAF), the South African Coal, Oil and Gas Corporation (SASOL), tractor manufacturers, commercial airlines, the South African Iron and Steel Industrial Corporation (ISCOR), the South African Transport Services (SATS) and large trucking firms as a diagnostic tool to monitor engine wear.

One of the earliest emission techniques used for the determination of additive elements in lubricating oils was that of Calkins and White (1946). They impregnated hot carbon electrodes by quenching them in oil so that the sample might subsequently be analysed by high voltage spark emission spectroscopy. A major breakthrough in the direct examination of oils came with the introduction of the rotating disc technique by Pagliassotti and Porche (1951). Later developments led to the direct current plasma (DCP) jet (Margoshes and Scribner, 1959). Although commercially available, the DCP jet in its original form did not fulfil its early promise. During the early 1960's a very rapid expansion of elemental analysis by atomic absorption spectrometry (AAS) took place and Sprague and Slavin (1963) proposed the use of AAS to determine some wear metals in used lubricating oils, without any prior ashing of the sample and by simply diluting the oils with suitable organic solvents.

Work by Greenfield et al. (1964) in England, and by Wendt and Fassel (1965) in the United States, on the application of the inductively coupled plasma (ICP) as an emission source greatly assisted atomic emission spectrometry (AES) in regaining its appeal as an analytical technique. Numerous features of the inductively coupled plasma source make it attractive for the analysis of organic samples (Greenfield and Smith, 1972) and the determination of wear metals and additives in new and used lubricating oils was demonstrated by Fassel et al. (1976).

1.1 Objective of the present study

More and more ICP instruments are being marketed worldwide and in South Africa with an ever increasing number of laboratories planning to use inductively coupled plasma atomic emission spectroscopy (ICP-AES) for the analysis of lubricating oils. For the most efficient and cost effective use to be made of a very expensive ICP atomic emission spectrometer, the optimum operating conditions for the plasma in the single-element and the multi-element mode must be established.

Optimization must produce an "analytically useful" plasma by using the net signal-to-background ratio (SBR) as the optimum response function, which should then yield excellent detection limits (Moore et al., 1984).

The versatility and speed of the sequential ICP emission spectrometer make it an ideal instrument for method development. The modified Simplex method used by Moore et al.

(1984) was used to optimise a 27 MHz all argon ICP for the analysis of 17 different elements present in lubricating oil as wear metals or contaminants and 4 other elements present in the most common additives in lubricating oil.

Performance characteristics of the ICP system, such as detection limit, analytical range, precision, accuracy and level of interference, achieved under the best compromise conditions, were determined and compared for both the standard cross flow and the high solids type nebulizers.

The final evaluation of the method was done by analysing a National Bureau of Standards (NBS) Standard Reference Material (SRM) and several round robin oil samples supplied by ISCOR.

CHAPTER 2: BACKGROUND AND LITERATURE SURVEY

This survey briefly outlines the use of inductively coupled plasma atomic emission spectrometry (ICP-AES) for the analysis of metals in lubricating oils and also provides a brief background to the development and use of the Simplex optimization method. Since many definitions of analytical parameters exist, a short outline is given of the definitions and formulae used during the course of this study.

2.1 Analysis of Oils by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

The analysis of metals in oils by ICP-AES has certain advantages over atomic absorption spectrometric methods owing to the higher temperatures involved and the longer residence time of the species in the plasma, in addition to its multi-element capability. For both ICP-AES and atomic absorption techniques, lubricating oils must be diluted with a suitable solvent before aspiration into a conventional nebulizer. Pforr and Aribot (1977) published the first paper on the direct introduction of oil samples, diluted with gasoline, into the plasma. Greenfield and Smith (1972) successfully determined Al, Cr, Cu, Fe, Ti, Ni, Mg and Mn in engine oil. However, neither of the authors provided any data on the accuracy and precision of their results.

Fassel et al. (1976) injected used synthetic jet engine lubricating oils diluted with 4 methyl-pentan-2-one (MIBK) (1/10; m/v) into the axial channel of an ICP-source and determinated 15 wear metals simultaneously. The reference solutions were prepared from Conostan organometallic standards (Conostan Division of the Continental Oil Company, Ponca City, Oklahoma, USA). Low and high viscosity oils could be accommodated without biasing analytical results. Very good agreement was obtained between the results achieved by ICP-AES and those reached by atomic absorption spectrometry (AAS). A comparison of analytical data for titanium by the ICP-AES method and by a "particle size independant" AAS procedure developed by Saba and Eisentraut (1977) also exhibited good correlation.

Merryfield and Loyd (1979) diluted lubricating oil with xylene (1/10; m/m) using Conostan standards for calibration. The NBS SRM1634 was also analysed with the results agreeing to within $\pm$ 2% of the certified values. Brown (1983), using typical sample dilutions of 1:10 (m/m) in xylene, found an overall precision for the determination of wear metals of between 5 and 10% and that for additives in lubricating oils between 2 and 5% at the 95% confidence level. Some interelement interferences were encountered but were corrected for. Evans and Klueppel (1985) developed an Automated Injection and Dilution System (unfortunately called AIDS) which allows the automatic delivery of a uniform, highly reproducible, diluted sample to the plasma, with a throughput of 80 samples per hour.

2.2 Simplex Method of Optimization

2.2.1 General survey

Apart from the unreliable and time-consuming "trial-and-error" method, several systematic techniques are available for the optimization of an ICP-AES system. As pointed out by Moore (1985), most of these are cumbersome, impractical for more than two variables and slow, or simply unsatisfactory.

The sequential Simplex method was first proposed by Spendley et al. (1962), and was followed by the modified Simplex method of Nelder and Mead (1965). The latter method is an improvement on the basic method in that the simplex can expand when moving in a favourable direction and contract when the direction of movement is unfavourable, allowing optimum conditions to be achieved more rapidly. Details of the modified Simplex method are not included here since they were reported in some detail by others (Moore, 1985; Morgan and Deming, 1974; Ebdon et al., 1980). The procedures and rules for the Simplex method used is given in Appendix I.

2.2.2. Computer programme

A computer programme called GENMOD. PROG (obtained from the Analytical Science Division, MINTEK, Randburg) was written for a 64K Apple IIe microcomputer. The programme allows for n variables ($1<n<11$), can be used for up to 20 analyte lines simultaneously, and has provision for up to 100 Simplex moves.

It allows a choice of three functions - net signal-to-background ratio (SBR), net signal, or minimum ionization interference. The programme has been successfully used in ICP-AES and also for the optimization of the graphite furnace technique in atomic absorption spectrometry (Moore, 1986). The programme has graphical displays used for monitoring, which also provide a permanent record of the complete optimization procedure. (Figure 1).

The most commonly used response function is the net signal-to-background ratio (SBR), since this should yield the lowest detection limits (Moore et al. 1984).

2.3 Analytical Parameters

Analytical parameters are the criteria against which the performance of an analytical method is tested. Some of these parameters which were used during this study, are briefly outlined here.

2.3.1 Analytical sensitivity

The relationship between the measured intensity, x, and the concentration, c. in $\mu g\ g^{-1}$ (or $\mu g\ cm^{-3}$) of the element to be determined is given by the calibration curve:

$$x = mc + i \quad - - - - - - - - - - - - - - - \quad (2.1)$$

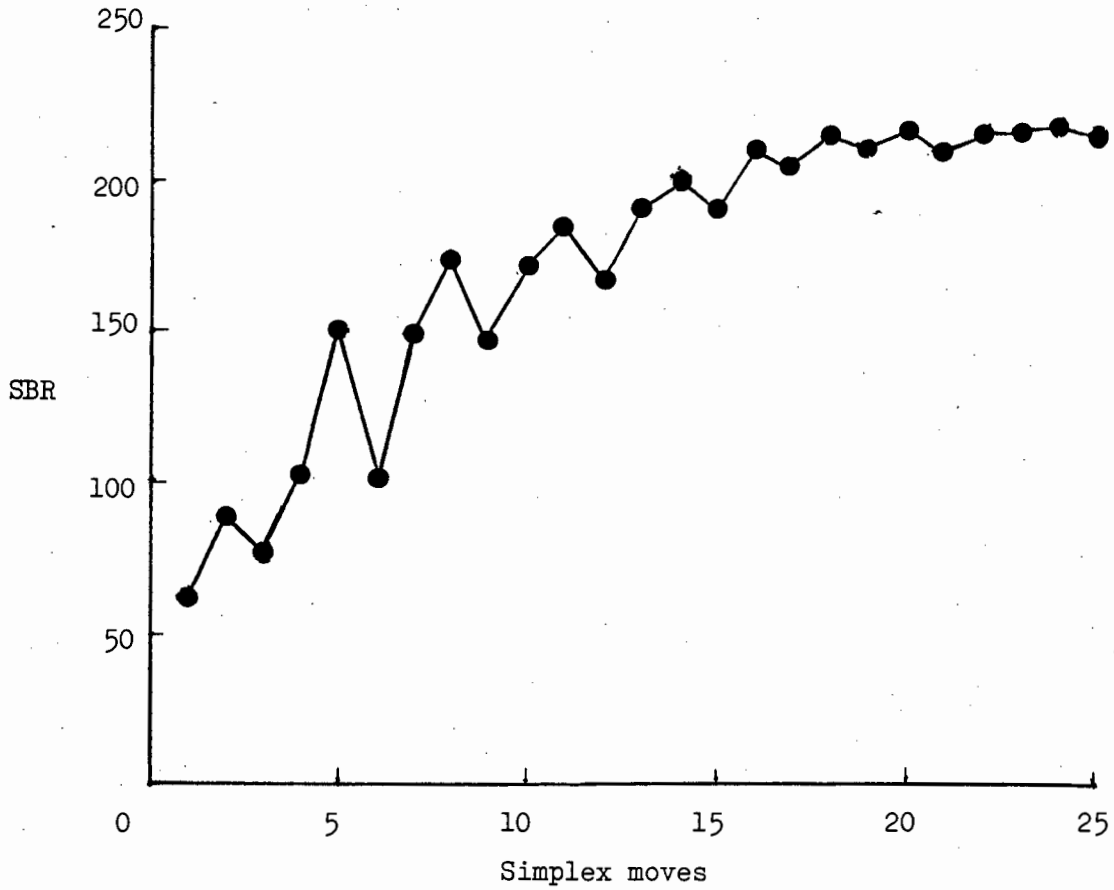

FIGURE 1 : Variation in net signal-to-background ratio (SBR)* with simplex moves for copper (324,754 nm).

*SBR for 10% oil in xylene (m/v) solution containing 10 µg cm^{-3} Cu.

where m is the slope or analytical sensitivity and i is the intercept (Long and Winefordner, 1983). The relationship between x and c is obtained by performing a linear regression analysis. The analytical sensitivity at each point on the calibration curve is therefore equal to the slope of the curve at that point.

2.3.2 Detection limit

The limit of detection is a number, expressed in concentration units that describes the lowest concentration level of the element that an analyst can determine to be statistically different from an analytical blank (Long and Winefordner, 1983). Although this definition appears straightforward, significant problems have been encountered in expressing these values because of the various approaches to the term "statistically different". In fact, calculated detection limits for an element can vary by an order of magnitude when different statistical approaches are applied. In defining detection limit (c_L) IUPAC (1978) states that

$$c_L = \frac{ks_B}{m} \qquad (2.2)$$

where k is a numerical factor chosen in accordance with the confidence level desired, s_B is the standard deviation of at least 20 blank readings and m is the analytical sensitivity (or slope of the calibration curve) of the spectral line. The use of k = 2 is the more popular choice (Fassel et al., 1976; Butler, 1983) and corresponds approximately to 95% confidence that some analyte is present or that the signal is

greater than $2s_B$. IUPAC (1978) suggested that k = 3 be used to allow a confidence level of 99,9%. It is also suggested by IUPAC (1978) that detection limit values be reported in all literature with their k value; c_L (k=3).

Winge et al. (1985) calculated an estimated value for the detection limit by making the "conservative" assumption that the relative standard deviation of the blank is 1%.

If the slope $m = \frac{I_n}{c}$ -(2.3)

where I_n is the net signal and c the concentration, then equation 2.2 can be written as follows:

$$c_L = \frac{k.s_B.c}{I_n} \quad \text{- - - - - - - - - - - - - - - - - - -(2.4)}$$

If k = 3, s_B = 0,01 I_b and I_n/I_b = net signal-to-background ratio, then :

$$c_L = \frac{3(0,01\ I_b)c}{I_n}$$

$$= \frac{0,03\ c}{I_n/I_b}$$

$$= \frac{0,03\ c}{SBR} \quad \text{- - - - - - - - - - - - - - - - - - (2.5)}$$

Butler (1983) pointed out that the detection limit can be determined from the precision versus concentration graph for any particular line. The detection limit values for k = 3 and k = 2 can be read off the graph at precision values of 33% and 50% respectively.

2.3.3 Analytical range

Butler (1983) defined the analytical working range as the concentration range in which the percentage relative standard deviation (% RSD) is better than or equal to three times the best % RSD over the given concentration range. Watling and Van Maarseveen (1980) defined the optimum working range as that range of concentrations over which the %RSD is always less than 2%, but pointed out that this choice may not be suitable for every analytical application and suggested that each analyst should determine the limits or analytical range for his own particular requirements. Boumans and Vrakking (1985) describe the minimum concentration required for quantitive determination as that corresponding to a signal-to-noise ratio of 10, i.e. a concentration equal to 5 to 10 times the detection limit (k = 3). An RSD of 10% is associated with this "limit of quantitive determination" or "lowest concentration of interest" (Boumans and Vrakking, 1985).

3. EXPERIMENTAL

3.1 Apparatus

All determinations, including the optimization and method development work, were performed using a Jarrell-Ash Atomscan 2400 sequential ICP-AES. A full description of the instrument is given in Appendix II. As mentioned, an Apple IIe computer was used for the Simplex optimization programme.

3.2 Reagents

Individual and composite Conostan "oil based organometallic standard solutions for the determination of metals in lubricating oil" were used for the preparation of stock solutions and working standards. A full description of these chemicals and the preparation of other standards is given in Appendix III.

3.3 Simplex Optimization of Instrumental Parameters

The following six variable parameters were selected for optimization of the plasma system; **forward power** (kW), **observation height** (mm above the load coil), **outer gas** (or coolant gas) **flow rate** ($dm^3\ min^{-1}$), **intermediate gas** (auxiliary or plasma gas) **flow rate** ($dm^3\ min^{-1}$), **carrier gas** (aerosol or inner gas) **flow rate** ($dm^3\ min^{-1}$) and **sample uptake rate** or feed rate ($cm^3\ min^{-1}$).

The modified Simplex method was applied to 17 individual spectral lines of elements present in oil (0 - 1000μg g^{-1}) and 4 individual spectral lines of elements present as additives (250 - 3000 μg g^{-1}) (See Table 2). Wavelength scans were obtained for several lines of each of the elements using a blank (metal free oil in xylene), a clean unused oil, a used oil, a 4,5 μg cm^{-3} composite Conostan C-21 standard and individual standards containing 100 μg cm^{-3} calcium, magnesium, phosphorous and zinc respectively. All solutions contained 10% (m/v) oil in xylene.

Wavelengths were chosen on the basis of sensitivity, linear range and minimal spectral or background interferences.

Optimization for all elements (Table 2) was done with the standard cross flow nebulizer (CFN) system, and was then repeated with the high solids nebulizer (HSN) system. The Apple IIe microcomputer using the GENMOD. PROG. programme described in section 2.2.2 was used for optimization.

In order to use concentrations which correspond approximately to the average concentrations expected in real samples, the 4,5 μg cm^{-3} composite standard was used for the wear metals while a clean unused oil (Honey Lube 20W50) containing high concentrations of Ca, Mg, P and Zn (100, 65, 135 and 160 μg cm^{-3} respectively after dilution) was used for the additives.

3.4 Determination of Analytical Parameters.

Net signal-to-background ratio, detection limit and analytical range were determined using compromise optimum conditions established in section 3.3 (Table 3).. A series of working standards were prepared in xylene from the intermediate standards mentioned in Appendix III.

The working standards ranged from 0,005 to 90,0 μg cm^{-3} for the wear metals and from 0,005 to 250 μg cm^{-3} for the additives. Metal free oil was added to each standard where necessary to maintain the same oil concentration (10% m/v) throughout the series. A blank was made up by diluting 10,00g of oil with xylene to 100,0 cm^3. Working solutions were stored in glass containers since xylene cannot be stored in most plastics. Analytical parameters were determined using the cross flow and the high solids nebulizers.

No background corrections were made but several inter-element corrections (IEC) were made. The correction factor; IEC, is calculated as follows:

$$IEC = \frac{\text{Interferent intensity/unit concentration of interferent}}{\text{Analyte intensity/unit concentration of analyte}} \quad - - - - - - - - - (3.1)$$

Corrected concentration = apparent concentration - IEC (concentration of interferent - - -(3.2)

A complete list of spectral lines used, intefering elements and inter-element correction factors are included in Table 2.

3.5 Determination of Wear Metal and Additive Concentrations in Used and Unused Lubricating Oils

Sample preparation

To evaluate what effect, if any, the wear particles have on the analytical response of the ICP, an unused oil was analysed employing two separate preparation methods.

In the first method, the used oil was shaken before the sample was withdrawn. The second method applied an ultrasonication step just prior to withdrawing the used oil from the sample vial. In both cases, 5,00 g of the sample was diluted with xylene to 50,00 cm^3.

Preparation of calibration standards

Calibration standards were prepared by placing a known mass of the 900 $\mu g\ g^{-1}$ intermediate standard of 21 elements in oil in a volumetric flask and diluting it to 100,0 ml with xylene. For the additives it was necessary to dilute the 2500 $\mu g\ g^{-1}$ intermediate standards. The diluted working standards ranged in concentration from 1,00 to 90,0 $\mu g\ cm^{-3}$ for the wear metals and from 1,00 to 250 $\mu g\ cm^{-3}$ for the additives. Metal free oil was added to each standard where necessary to maintain the

same oil concentration (10% m/v) throughout the series. The blank contained only 10% (m/v) metal free oil. Analytical conditions as listed in Table 3 were used with the high solids nebulizer system.

3.6 Determination of Metal Concentrations in NBS Standard Reference Material

NBS SRM1084 was prepared by placing 5,00 g of the sample in a volumetric flask and diluting it with xylene to 50,00 cm^3.

Calibration standards were prepared as described in section 3.5. The SRM was analysed using the same conditions as in section 3.5.

4. RESULTS AND DISCUSSIONS

4.1 Choice of Organic Solvent

Xylene and MIBK (4 methyl-pentan-2-one) were investigated as solvents for oil analyses. MIBK caused more difficulties in sustaining the plasma than xylene as confirmed by the high reflected power ($\pm$ 35W) as compared to the relatively low reflected power (<5W) while aspirating xylene thus confirming the findings of Varnes and Andrews (1978). Ward and Marciello (1978) investigated xylene, MIBK and chlorobenzene and found no significant difference in the detection limits obtained in these solvents but recommend xylene because of its "less objectionable aromatic odour".

The choice of solvent was also affected by the composition of the flow tubes. "Isoversinic" flow tubes were suitable for xylene but rapidly deteriorated when pumping MIBK. Maessen et al. (1984) reported similar problems with MIBK and suggested that free uptake be employed for this solvent, while Boorn and Browner (1982) suggested a syringe pump for the more polar solvents. (They also found that the limiting aspiration rate for MIBK is only about 75% of that of xylene).

Considering these factors, it was decided to use xylene as solvent.

It must, however, be emphasized that although the all argon plasma tolerates some organic solvents, their use necessitates a higher forward power, about 1,75 kW compared to about 1,0 kW used for aqueous solutions. This results in a heavier demand on the laboratory air conditioning system and reduces torch life.

4.2 Plasma Ignition

Four ignition procedures were established. Flow rates given here are for the cross flow nebulizer.

(a) After starting the outer (18 dm^3 min^{-1}) and intermediate (1,0 dm^3 min^{-1}) gas flows and setting the power at 1,0 kW, ignition is performed, whereafter the aerosol carrier gas flow (0,5 dm^3 min^{-1}) is started and water is nebulized while the matching network is manually tuned; then the power is raised to 1,7 kW and tuning is repeated. Subsequently, the intermediate gas flow is increased to 1,6 dm^3 min^{-1} and the matching network is retuned. The sample uptake rate is reduced to 0,2 cm^3 min^{-1} and at this stage, the liquid uptake tube is changed over to the organic solvent and, after retuning the network, the liquid uptake is gradually increased to about 1,2 cm^3 min^{-1} under constant tuning.

b) same as a) but automatic tuning is performed by instrument.

c) After starting the outer (18 dm^3 min^{-1}) gas flows and setting the power at 1,7 kW, ignition is performed whereafter the aerosol gas flow (0,5 dm^3 min^{-1}) is started, while tuning the matching network manually. Subsequently, the organic solvent is introduced at about 0,2 cm^3 min^{-1}. After retuning the network, the liquid uptake is gradually increased to about 1,2 cm^3 min^{-1} under constant tuning.

d) same as c) but automatic tuning is performed by instrument.

For the successful application of any of these procedures, it is imperative that initially not the slightest trace of organic material is present in the system. The presence of organic material caused over-arcing and the formation of streamers down the torch which probably caused damage to the torch.

The automatic tuning module is an optional accessory which was only installed midway during this project and proved most useful, not only resulting in easier start-ups but greatly improved plasma stability, particularly during sample change overs.

4.3 Choice of Wavelengths

Because a sequential spectrometer was used it was possible to investigate the suitability of all the available lines for each element. With the aid of spectral tables for ICP (Boumans, 1980; Winge et al., 1985; Wohlers, 1985; Parsons et al., 1980) the most prominent lines of each element were identified, together with possible interferences. Lines with

spectral interferences were eliminated where possible whereafter the lines giving the best SBRs were selected. Particular attention must be paid to the following:

Aluminium: The 308,215 nm line was selected since Mg and V interfere with the 309,298 nm line. This line, although not the most sensitive line, is also used by Fassel et al. (1976), Boumans and Lux-Steiner (1982) and Brown (1983).

Calcium, magnesium, phosphorus and zinc: Since these metals are usually present as additives in relatively high concentration, the less sensitive lines (except for P) were chosen to provide a somewhat longer linear range. The more sensitive lines for Mg and Zn are included in the list for wear metals.

Chromium, molybdenum and tin: Background shift enhancements from oils containing high Mg concentrations on the Cr, Mo and Sn spectral lines are illustrated in Figures 2 and 6. Fe interferes to some extent with B, Cd, Cr, Si, Zn and Mg while Cr seems to interfere strongly with the Sn line. Fortunately the Cr concentration is usually very low (< 20 $\mu g\ g^{-1}$ in undiluted oil).

Corrections for these and other less significant interferences (Figures 5 to 11) is accomplished by using the inter-element correction procedure included in the manufacturer software

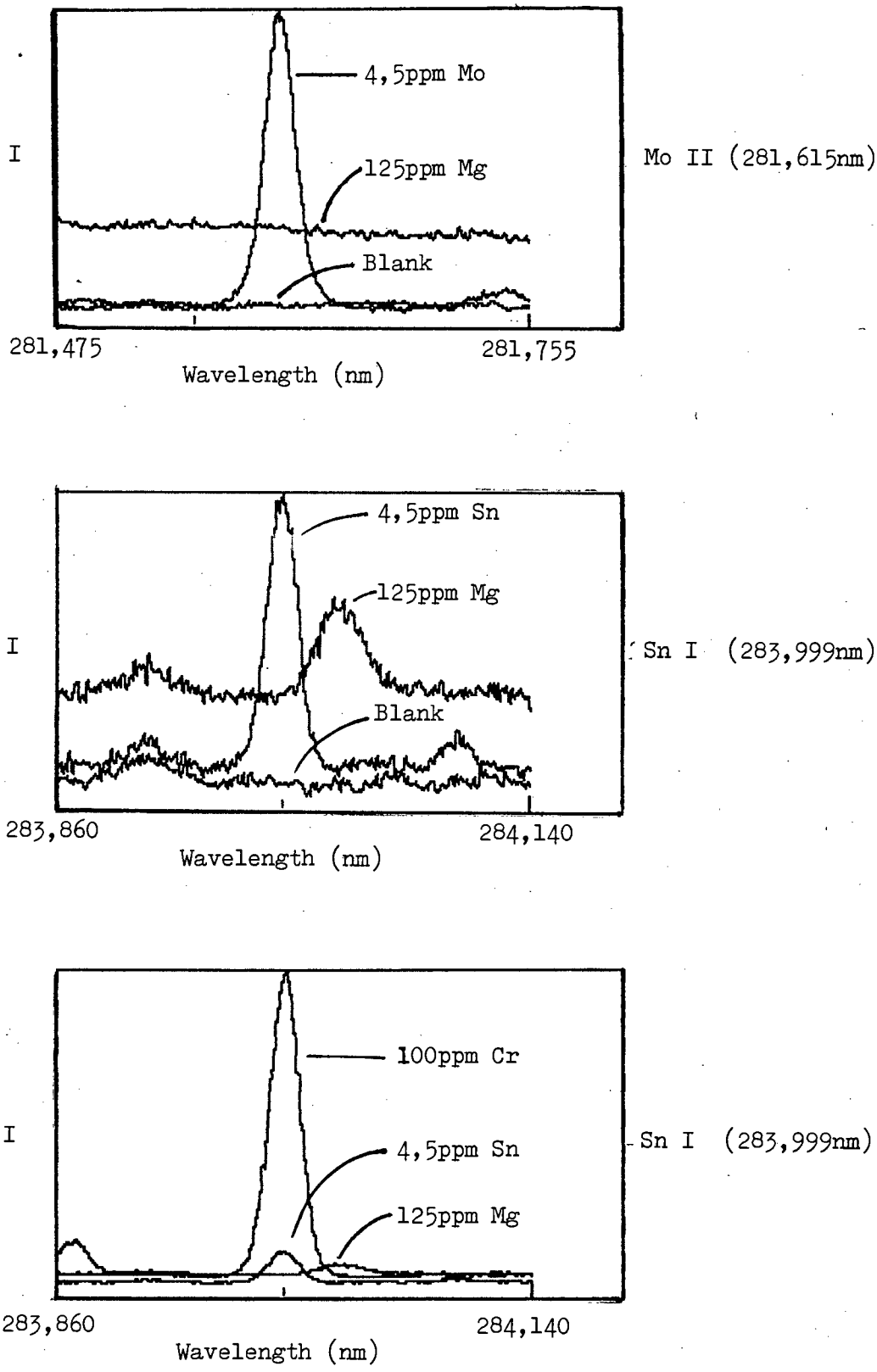

FIGURE 2 : Wavelength scans of the analysis lines for Mo and Sn.

package (Table 2). Correction for Mg is of particular importance since most internal combustion engine oils contain relatively high concentrations of Mg from additives.

4.4 Simplex Optimization

4.4.1 Preliminary measurements and boundary limits

Using Cu I (324,754 nm), Fe II (259,940 nm) and Mn II(357,610 nm) it was tentatively established in which respects the trends of the signal-to-background ratios (SBR) with the six ICP parameters differed from those for aqueous solutions, and over which ranges the parameters could be and had to be varied to embrace optimum conditions.

The setting of boundary limits is essential to the operation of the simplex method, since the simplex may otherwise move outside the permissable space and conditions beyond the instrument capabilities will be required. This phenomenon could, according to Moore (1985), possibly indicate physical constraints that limit the attainment of superior responses.

These preliminary investigations led to the following conclusions:

(a) Forward Power. In agreement with general experience (e.g. Fassel et al., 1976) a power level higher than for aqueous solutions is required to maintain a stable plasma. Below 1,4 kW the plasma is very weak and unstable, is easily

extinguished, and cannot be considered for routine analytical purposes. The upper limit was determined by the RF generator rating of 2,5 kW. The tests further indicated that the SBR varies considerably over the given range as shown in Figure 3(a).

(b) Outer Gas Flow Rate. It was found that for stable plasma operation a minimum flow of 16 dm^3 min^{-1} was required. The maximum flowrate of 20 dm^3 min^{-1} determined the upper limit. Flow rate adjustments could only be accurately measured to the nearest 0,5 dm^3 min^{-1}. However, Figure 3(b) shows that variation of flow rates between 17 and 20 dm^3 min^{-1} had only a marginal effect on the SBRs. This effect was also observed in aqueous media as observed by Ebdon (1986). It was therefore decided to fix the flow rate at 18 dm^3 min^{-1} for all further experiments. A flow rate of 18 instead of 19 dm^3 min^{-1} was chosen purely on grounds of economy.

(c) Intermediate Gas Flow Rate. It was found that the best SBRs are achieved for most elements with low intermediate gas flow rates. However, as reported by Boumans and Lux-Steiner (1982) the more carbonaceous matter introduced into the ICP, the higher the required flow rate. In contrast to the case when using aqueous solutions, it is not possible to decrease the intermediate gas flow to zero. In fact, flow rates below 1,5 dm^3 min^{-1} lead to a rapid build up of carbon deposits on the inner tube. Figure 3(c) shows the SRRs of five typical elements as a function of intermediate gas flow rate. The drastic increase in SBR shown by Cu and the drastic decrease

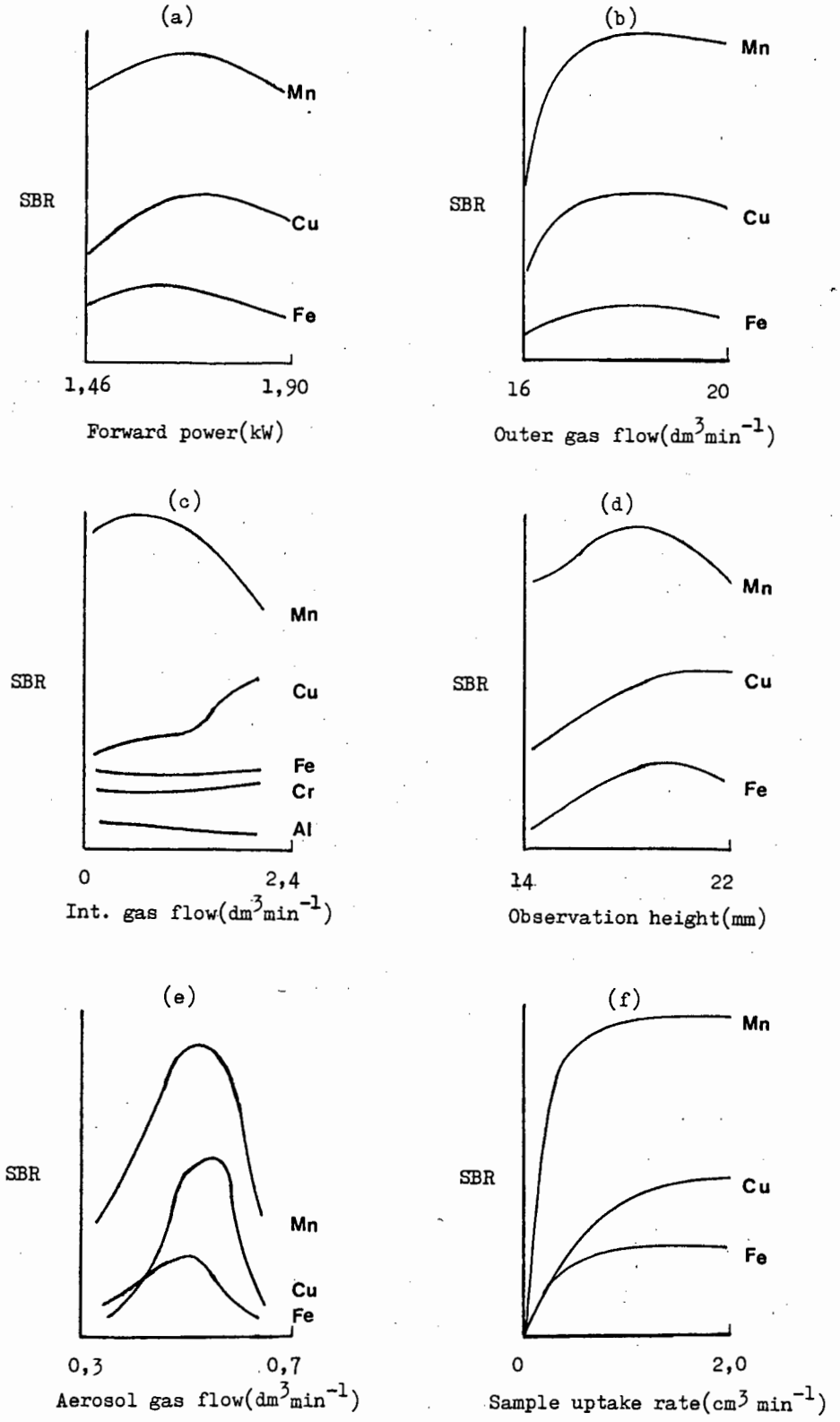

FIGURE 3 : Relative signal-to-background ratio as a function of various plasma parameters.

in SBR shown by Mn with increase in intermediate gas flow rate were proven to be exceptions as most other elements behaved as did Fe, Cr and Al. Due to these differences it was decided to include the intermediate gas flow rate in the final optimization. It is worth mentioning that although SBRs are generally higher at low intermediate gas flows, the background signal for all elements increases with a decrease in intermediate gas flow. Boundary limits were set between 1,0 and 2,2 $dm^3\ min^{-1}$. Intermediate gas flows in excess of 2,2 $dm^3\ min^{-1}$ tend to blow the plasma out of the torch.

(d) Observation Height. Measurement of signal-to-background ratio as a function of observation height (in mm above the load coil) can be performed between 10 and 26 mm. It is clear from Figure 3(d) that the optimum observation height for each element has to be carefully optimized. Background intensities generally decrease with increasing height in the plasma, as expected, resulting in optimum viewing heights between 15 and 21 mm above the load coil for both atom and ion lines.

(e) Carrier Gas Flow Rate. As shown by Figure 3(e), the carrier gas flow rate turned out to be one of the most crucial parameters. This parameter could be varied between 0 and 1,0 $dm^3\ min^{-1}$. Preliminary work was carried out with the cross flow nebulizer but later experiments using the high solids nebulizer showed similar effects.

(f) Sample Uptake Rate. This parameter seemed to have a very predictable effect as can be seen in Figure 3(f). The uptake rate is limited by the diameter of the flow tubing. The 1,0 mm tubing used with the cross flow nebulizer can deliver a maximum flow of 2,5 cm^3 min^{-1} while the 2,0mm tubing used with the high solids nebulizer can deliver 7,3 cm^3 min^{-1} when running the pump at maximum speed. The uptake rate required by the high solids nebulizer proved to be approximately double that required by the cross flow nebulizer shown in Figure 3 (f).

4.4.2 Simplex optimization of individual elements

The optimization based on the maximum SBR as the response function was performed for each of the individual lines listed in Table 2 using the standard cross flow nebulizer (CFN) and then repeated using the high solids nebulizer (HSN). The outer gas flow was kept constant throughout at 18 dm^3 min^{-1}.

The mean values (Tables 4 and 5) for the power, observation height and the flow rate of the intermediate gas show no significant variations although the individual values obtained for the two nebulizers differ slightly. This is due to normal statistical variation. The carrier gas flow rate and especially the sample uptake rate show a significant increase when using the high solids nebulizer. These increases are typical of Babington-type nebulizers.

It can be concluded that the high solids nebulizer does not necessarily introduce more sample into the plasma because the plasma required no extra power and the observation height as well as the intermediate gas flow required no significant alterations. Only the two parameters primarily associated with the nebulizer had to be altered.

The most significant aspect of the signal-to-background ratio's (Table 6) is the fact that the mean value for the high solids nebulizer is only slightly lower than that obtained for the cross flow nebulizer and that most individual values obtained are higher than those published by Winge et al. (1985) for aqueous solutions. If the value for Mg(279.553nm) is excluded, the mean values would be 77, 65 and 61 for the cross flow nebulizer, high solids nebulizer and the literature values (Winge et al., 1985) respectively. These values give a more meaningful reflection of the situation as the individual values for SBR are almost double those of the published values for most of the elements, with the exception of Mg(279,553nm). Although the cross flow nebulizer seems to give higher signals, it tends to become blocked by the small solid particles in used oil causing time-consuming delays.

4.4.3 Determination of compromise optimum conditions

The calculation of compromise conditions as an arithmetic mean of the individual optimum parameters does not give an adequate reflection of the "best" compromise conditions. A more objective basis for the calculation was used by Moore (1985).

This was done by the weighting of each analytical line in terms of the frequency of its current routine analytical usage (F) and relative SBR as follows:

$$\text{Weighting factor, } W = F/SBR \quad \text{- - - - - - - - - - - -(4,1)}$$

The application of these weighting factors to any parameter P of up to n elements gives the following expression for the compromise optimum parameter value, P_u :

$$P_u = \sum_{n}^{1}(W.P) \Big/ \sum_{n}^{1} W \quad \text{- - - - - - -(4,2)}$$

When using a sequential spectrometer, only the elements that have to be determined on a routine basis would be included in an analysis programme, in which case the frequency for all the elements in the programme would be the same. For the purpose of this study, the frequency of all the lines investigated were taken as one. Weighting factors were calculated for these lines, and the values for the compromise optimum parameters were computed. These values are shown in Table 7.

Table 6 gives a comparison of the SBRs obtained when the plasma was operated at the weighted compromise conditions and at the individual optimum conditions using the two different nebulizer systems. It is very clear from Table 6 that the adoption of the weighted compromise conditions led to a very small loss in SBRs for most elements. A maximum loss of 53%

occurs for AgI (328,065 nm). This seems to be in agreement with Moore (1985) who found that "soft" lines are more affected than "hard" lines by any changes in operating conditions.

Boumans and Lux - Steiner (1982), studying an argon cooled plasma, proposed that the 257,610 nm ionic line for manganese, although it is a "hard" line, can be regarded as being "representative" of all other lines. This was later confirmed by Moore et al. (1984).

A close examination of the compromise conditions shows that there is indeed a remarkable agreement between the best values for Mn II and the weighted compromise conditions obtained using both nebulizer systems.

The fact that the optima for individual values do not differ significantly from each other or from the weighted compromise conditions, tends to confirm the observations of Ebdon (1980), Boumans and Lux - Steiner (1982), Montaser et al. (1981) and Moore (1985), who averred that it might be less difficult to find compromise conditions with an all argon plasma than with an argon-nitrogen plasma.

4.5 Determination of Analytical Parameters.

Analytical parameters were restricted to the net signal-to-background ratio (SBR), detection limit c_L and the analytical

range. Sensitivity was omitted due to the fact that the value obtained varies with integration time and the voltage of the photo multiplier. The latter is selected by the instrument and depends on the concentration of the highest standard, the intensity of the line and the integration time used. It was decided that the net signal-to-backgound ratio would be a far more meaningful value to report for comparison purposes. The SBR values for the various systems used are shown in Table 6 and were discussed in the previous section.

4.5.1 Detection limit

As previously stated, this parameter can be determined through the use of several different methods. For the purpose of this study it was decided to apply the three most common and practical methods namely the IUPAC definition (eg 2.2), the method used by Winge et al. (1985) and Boumans and Lux-Steiner (1982) for better comparison, as well as the method used by Butler (1983). The results appear in Table 8. It must be borne in mind that the values are for the diluted oil (in xylene) and must be multiplied by 10 to find the corresponding value for the undiluted oil.

From the results it is clear that there is no significant difference between the values obtained in this work and those obtained by Boumans and Lux-Steiner (1982) for oil in MIBK and those published by Winge et al. (1985) for aqueous solutions.

The cross flow nebulizer seems to give slightly lower values than the high solids nebulizer. This is in agreement with the higher SBRs obtained using the former nebulizer.

The values in column "c" show the best agreement with the literature values. This is obviously due to the fact that they were all determined using the same formula (Winge et al., 1985) and making the same statistical assumption regarding the standard deviation of the blank. A close examination of the data obtained showed that the relative standard deviation of the blank is indeed greater than 0,01 or 1%. Some lines such as Al I (308,215nm), Fe II (259,940nm), P I (214,914nm) and Zn I (206,200nm) lines show values of almost 2% for the relative standard deviation of the blank while the V II (311,071nm) line has a value of only 0,7%. This variation in the value for s_B is the main reason for the differences between the detection limit values in columns "b" and "c". The values in column "a" which were determined according to Butler (1983) compare very well with the calculated values in column "b". The method according to Winge et al. (1985) is a very easy and rapid method of establishing an estimate of the detection limit but the IUPAC method is more realistic as it takes the actual variation of the blank into account.

4.5.2 Analytical range

By combining the two given definitions (Butler, 1983 and Watling and Van Maarseveen, 1980) the analytical range can be defined as the concentration range in which the percentage relative standard deviation (% RSD) is always better or less

than a previously determined value. This value for the %RSD will depend on the degree of precision required for the specific analysis. Typical precision obtained for the analysis of metals in oil have been reported as between 2-10% (Brown, 1983), 2-5% (Evans and Klueppel, 1985) and 2-6% (Fassel et al., 1976). By examining the results obtained in this work it is clear that precision is between 1,5 and 3,5% when working in the higher concentration ranges. This can be seen on the precision versus concentration graphs for the analytical lines investigated as shown in Figure 4 and Figures 12 to 16.

The precision obtained during the analysis of real samples were usually better than 5% and it was therefore decided to use 5% as the threshold value. It is quite clear from the precision versus concentration graphs that only the lower limit of the analytical range can be determined from these graphs. The upper limit is limited by the linearity of the calibration curve and the capabilities of the measuring system. Only by changing the sensitivity at higher concentrations (by applying a lower voltage over the photo multiplier) can the entire range be measured. Due to the limitations caused by calibration standards it was only possible to investigate up to 90 $\mu g\, g^{-1}$ for wear metals (900 $\mu g\, g^{-1}$ Conostan standard diluted 10x) and up to 250 $\mu g\, g^{-1}$ (2500 $\mu g\, g^{-1}$ Conostan standards diluted 10x) for the additives. This covers the range adequately since wear metals are usually

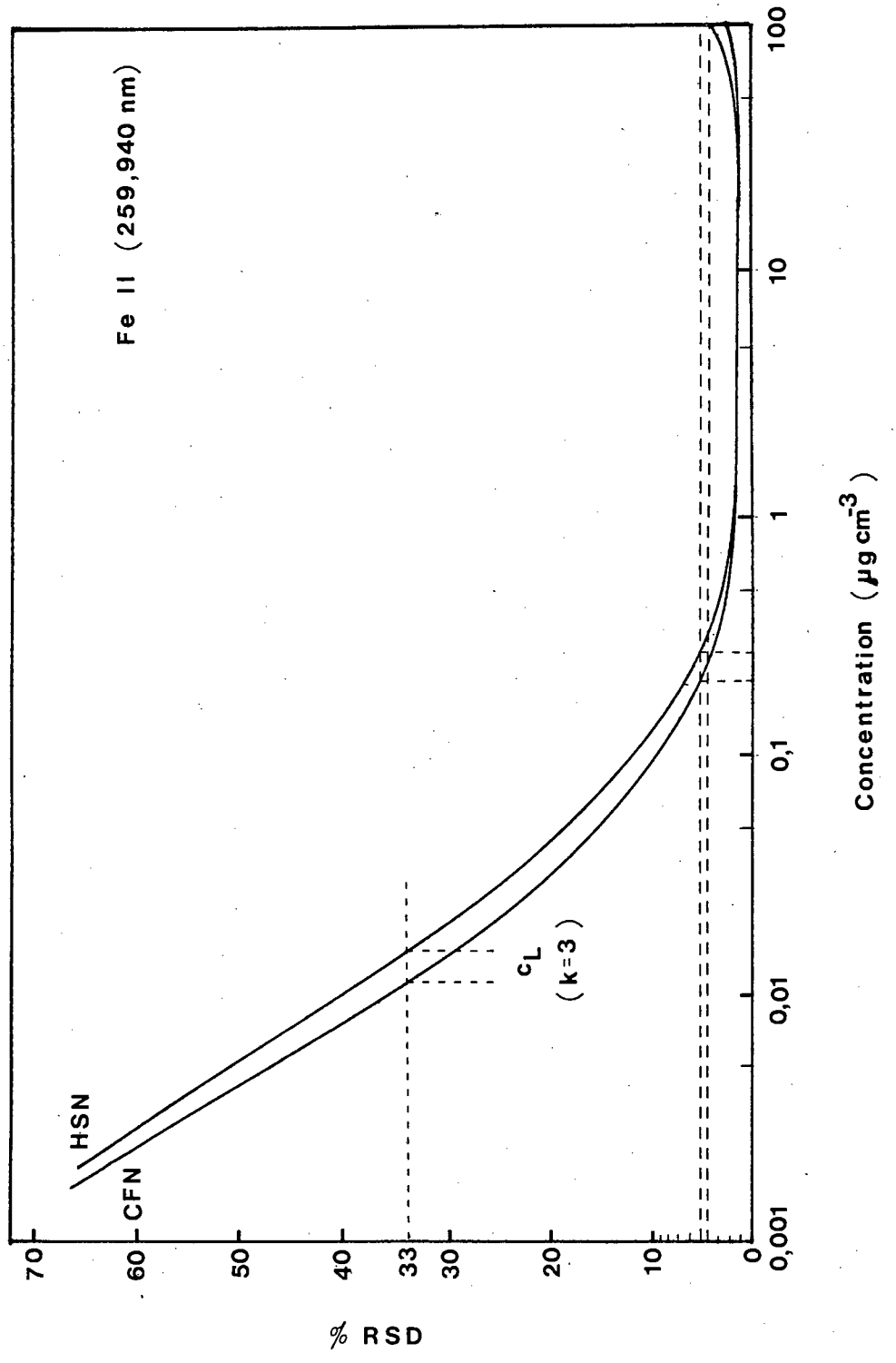

FIGURE 4 : Precision vs. concentration graphs for iron using the high solids nebulizer (HSN) and cross flow nebulizer (CFN).

present in the concentration range of 0 - 1000 μg g^{-1}(in undiluted oil) but may sometimes go up to 1500 or 2000 μg g^{-1} when excessive wear takes place. Additive concentrations range between 250 and 3000 μg g^{-1}.

Calibration curves for all elements were found to be linear over the entire range as required. It is therefore only possible to report the lower limit of the analytical range. It is proposed that this parameter be called the limit of determination, c_D, as apposed to the "lowest determinable concentration" proposed by Fassel et al. 1976 and the "limit of quantitative determination" by Boumans and Vrakking (1985). The latter authors also called this quantity the limit of determination and show that it will always be in the range between $5c_L$ and $10c_L$.

Table 9 shows the limits of determination obtained for all the lines under investigation using the two different nebulizer systems at a 4% and a 5% level of precision. These values follow the same pattern as the detection limits shown in Table 8.

By calculating a mean value for the detection limits obtained using the IUPAC definition and a mean value for the limit of determination for both nebulizers the following ratios were established:

at the 5% RSD level: c_D/c_L (HSN) = 9,8 ≈ 10

c_D/c_L (CFN) = 8,9 ≈ 9

at the 4% RSD level: c_D/c_L (HSN) = 12,9 ≈ 13

c_D/c_L (CFN) = 10,8 ≈ 11

From this it is clear that a general rule regarding the c_D/c_L ratio cannot be defined. c_D depends entirely on the precision required and can only be determined experimentally by plotting a precision versus concentration graph from which c_D can be determined.

Another interesting observation from the precision versus concentration graphs is that the cross flow nebulizer tends to have the best precision at concentrations lower than the limit of determination (16 of the 21) but that the high solids nebulizer has the same or better precision over the higher concentration range (with the exception of Al I).

Table 10 shows the analytical ranges obtained for the various analytical lines for the analysis of metals in lubricating oil by ICP-AES using xylene as solvent. It is very clear that the vast majority of used and unused lubricating oil samples could be analysed with very good precision. This is also the case for the samples with concentration levels above the working range. If these values are compared with those obtained for atomic absorption spectrometry (Marais, 1982) in Table 11, it is very clear that ICP has much lower limits of determination for some elements like aluminium and silicon

(almost an order of magnitude) while for the other elements it is almost the same. The real advantage of the ICP however, is the astoundingly dynamic analytical range making it possible to analyse samples over a wide concentration range without time wasting dilutions. The best examples of this being all the additives (calcium, magnesium, phosphorous and zinc) as well as the wear metals copper and iron which often have concentrations in excess of 500 $\mu g\ g^{-1}$.

Aluminium and silicon are usually present at lower levels (0-40$\mu g\ g^{-1}$) resulting in poor precision when using AAS.

4.5 Analysis of Lubricating Oils

4.5.1 Sample preparation

Used lubricating oils usually contain some particulate matter which makes it very difficult to take an homogeneous sample for the analysis since the particles tend to settle out. Thorough manual shaking works well unless high viscosity oils are used, the sample containers are very full or when sludge deposits are present.

Preliminary analyses showed that the sample taking procedure was one of the main reasons for variation in results.

To investigate this, a sample was withdrawn before shaking, after vigorous manual shaking and after ultrasonicating the sample in its original plastic bottle for 20 minutes. This

procedure was repeated on three different samples leading to very interesting results (Table 12). The upward trend in element concentration from simple shaking of the used oil to ultrasonicating indicates a particle distribution effect. It is evident from these results that ultrasonication causes a significant improvement, confirming the findings of Brown (1983). This improvement has particular significance for the analysis of Fe and Si which are the major contributors to the particulate matter in used oils.

Ultrasonication was used throughout for all subsequent analyses.

4.5.2 Analytical results

To determine the accuracy of metal analyses in new and used lubricating oils, both a standard reference material and several "round robin" samples were analysed. The results for several elements in NBS SRM1084 (Wear Metals in Lubricating Oil) are given in Table 13. This standard reference material contains no metal particles. The results show excellent agreement between the certified (or true) values and the mean obtained for ten separate determinations for all elements except for magnesium (the student t-test was applied at the 95% confidence level). The reason for this difference could not be established since the analysis was repeated several times using two different Conostan standards (900$\mu g\ g^{-1}$ C-21 composite standard and a 5000 $\mu g\ g^{-1}$ magnesium standard) giving the same results.

The SRM was blended and bottled in 1979 and it is possible that Mg is not stable over an 8 year period. This suspicion was confirmed to some degree when two old working standards (1,00 and 10,0 μg cm^{-3} composite standard in xylene) that were kept in a glass container for approximately 1 year were analysed using fresh standards. The results, which can be seen in Table 14, clearly show that the lower concentration standard (1,00 μg cm^{-3}) deteriorated by almost 90% for Mg while the other elements analysed show only some statistical variations. The magnesium concentration of the higher standard decreased by only 5% (which confirms the general belief that lower standards have a much shorter shelf life than higher standards). The most significant aspect of these results is however the remarkable stability shown by all the other elements analysed.

Several typical oil samples of varying type and viscosity were obtained from ISCOR. These samples were analysed and the results compared with one set of results supplied by ISCOR using AAS. Very poor agreement was obtained which led to the preparation of a single round robin sample (engine oil HQTS1). This sample was sent out to six ISCOR laboratories using AAS as well as the SAAF and a commercial analytical laboratory (Wearcheck (Pty) Ltd., Pinetown, Natal) who use AES with a rotating disc electrode (RDE). The results (including the results from this laboratory using ICP-AES) are shown in Table 15. Although there is some agreement, described as "within

the tolerances expected of the technique" (Sidiropoulos, 1987) it is noteworthy that the ICP-AES results are very close to the mean.

"Round robin" sample HQTS1 was prepared by mixing a used engine oil with Conostan C-21 standard and therefore contained a relatively small amount of particulate matter. It can be assumed that good agreement should be obtained between AAS and AES. This, however, is not always the case when samples with larger amounts of particulate matter are analysed since the relatively colder flame used by AAS does not atomise particles as readily as the much hotter plasmas of AES. Thirteen used lubricating oils of different type and viscosity were obtained from ISCOR. These samples were analysed by the ISCOR laboratories using AAS, the SAAF oil analyses laboratories and a commercial oil laboratory (Wearcheck) using spark rotrode AES and by ICP-AES using the method and optimum conditions described earlier.

From the results (Table 16) it is clear that atomic absorption spectrometry cannot "compete" with the atomic emission spectrometric techniques for the analysis of oils with high iron and/or silicon content. The higher temperatures involved and the longer residence time of the species in the plasma must clearly be responsible for the more efficient atomization of the larger particulate matter in the oil.

The large variation in some of the results, particularly between the emission techniques, can be attributed to various possible causes:

- The SAAF instrument is optimised for the analysis of aircraft oils which do not contain any Ca - additives. All Ca-containing oils cause a spectral interference on some of the other elements such as Al, Cu, Fe and Si.

- Poor or inconsistent sampling

- Sample transportation into the flame or plasma differs greatly for the three techniques causing variations in the results merely from varying viscosity and/or particle size within the samples. Despite this, a successful wear metals monitoring programme may be conducted provided the same sample preparation procedure and technique is used throughout the engine test.

It was most interesting to note that the Fe concentration determined by ICP-AES was approximately the same or higher than those by rotrode - AES. This is in agreement with the findings of Brown (1983) (although he analysed only one sample!).

5. CONCLUSIONS

The application of an argon-cooled inductively coupled plasma atomic emission spectrometer for the analysis of metals in lubricating oils was investigated. In order to make the most efficient and cost effective use of the ICP-atomic emission spectrometer the modified Simplex optimization technique was successfully applied to determine optimum operating conditions for 21 elements. It was found that optimization on a representative line such as the 257,610 nm ionic line for manganese is a rapid means for the establishment of compromise conditions for multi element analysis without a significant loss in the SBR.

The detection limits reported here for oil in xylene are of the same order as the published limits for aqueous as well as oil in MIBK solutions. However, analytical range tests, as defined in this study, indicate that the most valuable property of the ICP system is not the excellent limits of detection, but the astounding dynamic analytical range. This allows determinations to be made over a large concentration range without the use of serial dilutions.

Two different nebulizer systems were investigated and although the cross flow nebulizer seems to give slightly higher sensitivities, it blocks rapidly when analysing used oil

samples. The high solids nebulizer on the other hand, uses much more sample (approximately 3 times) but can be used for long periods without blockage.

Particle size affects the analysis of wear metals in used oils. The size of wear particles may change during the operation of an engine. This would give rise to random fluctuations of wear metal concentrations throughout the operation of the engine creating imprecision in the analyses. Despite this, a successful wear metals monitoring programme may be conducted provided the same sample preparation procedure is used throughout the engine test.

Based on an evaluation of the literature and on the experience gained in this study, ultrasonication of the oil sample is recommended before withdrawing the analytical sample.

Results from the analysis of an NBS standard reference material and a round robin used oil showed the ICP-AES to be a very accurate method for the analysis of metals in oil. This was confirmed by the results of several used oil samples of varying type and viscosity which all showed good agreement with established techniques such as the spark-rotrode- AES.

Owing to the higher temperatures involved and the longer residence time of the species in the plasma, wear metals analyses by ICP-AES have many advantages over AAS. In addition to the more efficient atomisation of particulate

matter the multielement capabilities of the ICP enable more samples to be analysed in any given time thus providing a more cost efficient service.

ICP-AES has several advantages over spark-rotrode-AES:

1. ICP-AES generally has better precision and lower detection limits.

2. The running cost of an ICP-AES is lower (± R10 per hour for argon) than that of a spark - rotrode - AES (± R50 per hour for electrodes).

3. A simultaneous ICP-AES can be operated with an auto sampler analysing between 80 and 100 samples per hour, leaving the technician free to do other tasks while the spark-rotrode AES needs manual attention for each sample.

Since the analysis of wear metals in used lubricating oil is mainly concerned with establishing a wear pattern and not in the absolute values of any given element present, the author is of the opinion that ICP-AES can be successfully applied to the analysis of metals in lubricating oils. Inductively coupled plasma-atomic emission spectrometry has speed, accuracy and precision which at least equals, and probably improves upon any of the more established techniques.

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TABLE 1 : Metals analysed in lubricating oils and possible trouble areas in engines (from McKenzie, 1981)

Element		Possible trouble areas
Aluminium	Al	pistons (aircraft engines), bearings (Al-Sm), push rods, air coolers, pump housings, oil pumps, gear casings
Chromium	Cr	cylinder liners, piston rings, alloyed steel, coolant leaks, seal rings (jet engines), plating on compression rings, chromate (cooling system)
Copper	Cu	bearings, bushes, (Cu-Pb-Sn), sleeves, bearing cages, coolant core tubes, valve guides, thrust washers (alloyed with S, Ti)
Iron	Fe	piston rings, ball and roller bearings, gears, pump gears, cylinder liners, valve guides, rust
Lead	Pb	bearings (Pb-Sn, Cu-Pb-Al), thrust bearings (Cu-Pb), bearing cages, bearing retainers (alloyed with Cu, Ti), tetra ethyl lead in petrol engines (anti knock)
Silicon	Si	air-borne dust, seal materials, silicon lubricant (jet engines)

TABLE 2 : Wavelengths used for the analysis of wear metals (1-17) and additives (18-21) in lubricating oil

	Element	Wavelength (nm)	Interfering element and correction factor*
1.	Ag I	328,068	-
2.	Al I	308,215	-
3.	B I	249,773	Fe (0,000731)
4.	Cd I	228,802	Fe (0,00107)
5.	Cr II	283,563	Fe (0,00216); Mg (0,00120)
6.	Cu I	324,754	-
7.	Fe II	259,940	-
8.	Mg II	279,553	-
9.	Mn II	257,610	-
10.	Mo II	281,615	Mg (0,00949)
11.	Ni I	221,647	-
12.	Pb II	220,353	-
13.	Si I	251,612	Fe (0,00683)
14.	Sn I	283,999	Mg (0,012); Cr (0,429)
15.	Ti II	334,941	-
16.	V II	311,071	-
17.	Zn I	213,856	Cr (0,00177); Fe (0,00326)
18.	Ca I	422,673	-
19.	Mg I	285,213	Fe (0,00244); Cr (0,00144)
20.	P I	214,914	Cu (0,00193)
21.	Zn II	206,200	Cr (0,00191)

*Inter-element correction factors were calculated using equation 3.1

TABLE 3 : Instrumental conditions for the determination of metals in oil

	Nebulizer	
	Cross flow	High solids
Forward Power (kW)	1,72	1,71
Observation Height above coil (mm)	18,1	18,1
Outer Gas Flow Rate ($dm^3\ min^{-1}$)	18,0	18,0
Intermediate Gas flow Rate ($dm^3\ min^{-1}$)	1,65	1,65
Carrier Gas Flow Rate ($dm^3\ min^{-1}$)	0,48	0,54
Sample uptake Rate ($cm^3\ min^{-1}$)	1,2	3,1

Rinse time : 30 s

Integration Time : 1,5 s for wear metals

1,0 s for additives

10 s for the determination of detection limits

Background correction : None

Inter-element corrections : Corrections were made as indicated in Table 2.

TABLE 4 : Optimum plasma parameters to give maximum SBRs using the standard cross flow nebulizer (CFN)

Element	Power kW	Observation height mm	Flow rate of intermediate gas $dm^3\ min^{-1}$	Flow rate of carrier gas $dm^3\ min^{-1}$	Sample uptake rate $cm^3\ min^{-1}$
Ag I	1,46	18,1	1,7	0,50	1,2
Al I	1,62	19,1	1,8	0,55	1,4
B I	1,64	20,0	1,5	0,50	1,0
Cd I	1,46	17,2	1,7	0,45	0,8
Cr II	1,70	18,2	1,8	0,49	1,2
Cu II	1,58	21,0	1,8	0,54	1,5
Fe II	1,61	19,3	1,7	0,51	1,4
Mg II	1,66	19,4	1,3	0,52	1,2
Mn II	1,68	18,1	1,5	0,52	1,2
Mo II	1,70	14,2	1,7	0,43	1,2
Ni II	1,70	17,4	1,2	0,46	1,2
Pb I	1,69	17,6	1,6	0,42	1,0
Si I	1,68	19,2	1,5	0,50	1,2
Sn I	1,74	19,9	1,7	0,51	1,2
Ti II	1,70	18,0	1,6	0,49	1,4
V II	1,86	20,1	1,7	0,50	1,2
Zn I	1,70	18,6	1,4	0,45	1,2
Ca I	1,62	17,7	1,4	0,52	1,2
Mg I	1,76	18,6	1,4	0,48	1,2
P I	1,80	17,5	1,2	0,45	1,2
Zn II	1,74	15,8	1,4	0,40	1,2
Mean	1,67	18,3	1,55	0,49	1,2

TABLE 5 : Optimum plasma parameters to give maximum SBRs using the high solids nebulizer (HSN)

Element	Power kW	Observation height mm	Flow rate of intermediate gas $dm^3\ min^{-1}$	Flow rate of carrier gas $dm^3\ min^{-1}$	Sample uptake rate $cm^3\ min^{-1}$
Ag I	1,50	18,2	1,7	0,57	3,6
Al I	1,60	19,0	1,7	0,62	3,6
B I	1,67	20,3	1,5	0,64	5,5
Cd I	1,47	17,3	1,7	0,50	2,5
Cr II	1,65	18,4	1,8	0,53	2,5
Cu II	1,57	20,6	1,8	0,63	4,4
Fe II	1,66	19,5	1,7	0,56	2,5
Mg II	1,67	19,0	1,4	0,55	2,5
Mn II	1,68	18,0	1,5	0,55	3,0
Mo II	1,72	15,0	1,7	0,53	2,5
Ni II	1,69	17,8	1,2	0,48	2,5
Pb I	1,68	17,3	1,6	0,52	3,0
Si I	1,69	19,0	1,5	0,58	3,6
Sn I	1,74	19,8	1,7	0,52	3,6
Ti II	1,72	18,2	1,6	0,60	2,5
V II	1,85	20,6	1,6	0,55	2,5
Zn I	1,71	18,7	1,4	0,50	2,5
Ca I	1,62	17,9	1,4	0,55	3,6
Mg I	1,75	18,2	1,3	0,58	3,0
P I	1,78	17,3	1,2	0,53	3,0
Zn II	1,76	16,0	1,4	0,48	2,5
Mean	1,67	18,4	1,54	0,55	3,1

TABLE 6 : Comparison of SBRs obtained using individual optimum conditions and weighted compromise conditions

Element	Wavelength	Net signal-to-background ratio (SBR)*				Lit
		Individual optima		Compromise conditions		
		CFN	HSN	CFN	HSN	
Ag I	328,068	105	128	69	61	38
Al I	308,215	13	11	11	10	7
B I	249,773	24	19	24	18	63
Cd I	228,802	64	61	61	47	110
Cr II	283,563	90	87	89	40	42
Cu II	324,754	165	215	126	157	56
Fe II	259,940	101	79	84	58	48
Mg II	279,553	1 462	1 331	1 020	959	1 950
Mn II	257,610	456	441	454	438	220
Mo II	281,615	28	21	25	15	21
Ni I	221,647	24	24	23	18	29
Pb II	220,353	5,3	4,8	4,8	4,3	7
Si I	251,612	37	40	36	37	25
Sn I	283,999	10	10	7,5	7,0	3
Ti II	334,941	233	184	157	125	79
V II	311,071	95	62	71	45	30
Zn I	213,856	74	65	70	51	170
Ca I	422,673	56	25	32	13	30
Mg I	285,213	237	175	166	107	190
P I	214,914	3,5	4,1	2,2	2,6	4
Zn II	206,200	49	50	32	43	51
Mean		159	145	122	108	151

CFN : Cross flow nebulizer
HSN : High solids nebulizer
Lit : Winge et al. (1985)

*SBR for 10 % oil in xylene (m/v) solutions containing 10 $\mu g\ cm^{-3}$ of each element.

TABLE 7 : Compromise optimum parameters for 21 elements

Parameter		Value*	
		CFN	HSN
1. Forward power	(kW)	1,72	1,71
2. Observation height above coil	(mm)	18,1	18,1
3. Flow rate of outer gas	(dm^3 min^{-1})	18**	18**
4. Flow rate of intermediate gas	(dm^3 min^{-1})	1,45***	1,47***
5. Flow rate of carrier gas	(dm^3 min^{-1})	0,48	0,54
6. Sample uptake rate	(cm^3 min^{-1})	1,2	3,2

*CFN : Cross flow nebulizer

HSN : High solids nebulizer

**Flow rate of outer gas was fixed at 18

***Flow rate of intermediate gas was adjusted to 1,65 dm^3 min^{-1} for all determinations to avoid carbon build up (see Table 3).

TABLE 8 : Comparison of detection limits attained in this work using various methods and detection limits reported in literature

Spectral line (nm)	Detection limits (k = 3) (ng cm^{-3})							
	This work (10 % m/v oil in xylene)						Literature	
	High solids nebulizer			Cross flow nebulizer				
	a	b	c	a	b	c	MIBK	Water
Ag I 328,068	2,7	3,3	4,9	2,1	2,9	4,3	2,0	7,0
Al I 308,215	34	51	30	20	41	27	20	45
B I 249,773	30	16	17	18	12	13	5,0	4,8
Cd I 228,802	9,0	11	6,4	7,6	8,0	4,9	4,0	2,7
Cr II 283,563	8,0	6,4	4,1	17	6,4	4,1	3,0*	7,1
Cu II 324,754	11	2,2	1,9	7	2,7	2,4	1,0	5,4
Fe II 259,940	15	7,0	5,2	11	4,1	3,6	3,0	12
Mg II 279,553	0,6	0,55	0,31	0,5	0,32	0,29	0,06	0,15
Mn II 257,610	0,55	0,7	0,68	0,5	0,68	0,66	0,3	1,4
Mo II 281,615	30	30	20	25	19	12	8,0	14
Ni I 221,647	33	36	17	23	28	13	15	10
Pb I 220,353	180	120	70	110	107	64	70	42
Si I 251,612	11	8,9	8,1	12	9,4	8,3	50	12
Sn I 283,999	135	45	42	120	95	40	3,0*	111
Ti II 334,941	2,2	2,5	2,4	2,5	2,2	1,9	3,0*	3,8
V II 311,071	5,0	3,9	6,7	2,1	2,4	4,2	-	10
Zn I 213,856	5,9	2,6	5,9	10	6,2	4,3	4,0	1,8
Ca I 422,673	25	22	23	1,0	8,6	9,4	-	10
Mg I 285,213	1,8	1,6	2,8	0,9	1,0	1,8	-	1,6
P I 214,914	350	300	115	350	400	136	80	76
Zn II 206,200	15	15	7,0	27	20	9,4	-	5,9

MIBK - Oil in MIBK : Boumans and Lux-Steiner (1982)
Water - Aqueous solutions : Winge *et al.* (1985)
a - Determined from precision vs concentration graph at 33 % RSD
b - Calculated according to IUPAC formula : $C_L = 3 \times S_{b/m}$
b - Calculated according to Winge *et al.* (1985) : $C_L = 0,03\ C/SBR$
*Fassel *et al.* (1976)

TABLE 9 : Comparison of lower limits of determination attained using the high solids nebulizer (HSN) and the cross flow nebulizer (CFN) at different levels of precision

Spectral line (nm)		Limit of determination (ng cm^{-3})			
		High solids nebulizer		Cross-flow nebulizer	
		4 % RSD	5 % RSD	4 % RSD	5 % RSD
Ag I	328,068	70	57	60	50
Al I	308,215	800	600	580	460
B I	249,773	670	550	1 000	790
Cd I	228,802	200	140	130	100
Cr II	283,563	110	90	160	120
Cu II	324,754	80	70	46	38
Fe II	259,940	400	300	300	230
Mg II	279,553	21	17	21	16
Mn II	257,610	44	58	30	36
Mo II	281,615	450	380	150	120
Ni I	221,647	440	330	300	230
Pb II	220,353	900	1 100	750	800
Si I	251,612	400	310	720	560
Sn I	283,999	1 400	1 200	740	580
Ti II	334,941	43	35	54	43
V II	311,071	91	70	60	42
Zn I	213,856	170	130	90	70
Ca I	422,673	380	280	320	220
Mg I	285,213	160	120	90	63
P I	214,914	3 700	3 000	2 800	2 300
Zn II	206,200	470	350	600	430

TABLE 10 : Analytical range for the analysis of metals in lubricating oil by ICP-AES

Spectral line (nm)		Analytical range ($\mu g\ g^{-1}$)*	
		High solids nebulizer	Cross flow nebulizer
Ag I	328,068	0,6 - 1 000	0,5 - 1 000
Al I	308,215	6,0 - 1 000	4,6 - 1 000
B I	249,773	5,5 - 1 000	7,8 - 1 000
Cd I	228,802	1,4 - 1 000	1,0 - 1 000
Cr II	283,567	0,9 - 1 000	1,2 - 1 000
Cu II	324,754	0,7 - 1 000	0,4 - 1 000
Fe II	259,940	3,0 - 1 000	2,3 - 1 000
Mg II	279,553	0,2 - 1 000	0,2 - 1 000
Mn II	257,610	0,6 - 1 000	0,4 - 1 000
Mo II	281,615	3,8 - 1 000	1,2 - 1 000
Ni I	221,647	3,3 - 1 000	2,3 - 1 000
Pb II	220,353	11 - 1 000	8 - 1 000
Si I	251,612	3,1 - 1 000	5,6 - 1 000
Sn I	283,899	12 - 1 000	5,8 - 1 000
Ti II	334,941	0,4 - 1 000	0,4 - 1 000
V II	311,071	0,7 - 1 000	0,4 - 1 000
Zn I	213,856	1,3 - 1 000	0,7 - 1 000
Ca I	422,673	2,8 - 2 500	2,2 - 2 500
Mg I	285,213	1,2 - 2 500	0,6 - 2 500
P I	214,914	30 - 2 500	23 - 2 500
Zn II	206,200	3,5 - 2 500	4,3 - 2 500

*Concentrations noted in this table refer to the levels in the undiluted oil before the 1 : 10 m/v dilution.

The lower limit of the range was determined by using a 5 % RSD as threshold value while the upper limit was limited by the concentration of the highest standards.

TABLE 11 : Analytical range for the analysis of metals in lubricating oil using atomic absorption spectrometry and MIBK as solvent (Marais, 1982)

Spectral line (nm)		Analytical range ($\mu g\ g^{-1}$)*
Al	309,4	27 - 870
Cr	357,9	3,4 - 76
Cu	324,8	0,6 - 59
Fe	248,5	3,4 - 75
Pb	217,1	1,1 - 110
Si	251,7	40 - 2 222

*Concentrations noted in this table refer to the levels in the undiluted oil before the 1 : 10 v/v dilution.

The lower limit of the range was determined by using a 5 % RSD threshold value while the upper limit was limited by excess curvature in the calibration curve.

TABLE 12 : Effect of sample preparation on the analytical response of the ICP

Sample	Method	Concentration ($\mu g\ g^{-1}$)				
		Al	Cu	Fe	Pb	Si
2152	No shaking	11	95	47	5,3	9
	Manual shaking	16	96	149	6,0	19
	Ultrasonicated	15	100	184	6,3	45
	AES (SAAF)	40	163	200	9	31
	AES (Wearcheck)	16	232	143	2	8
2171	No shaking	1,0	7,2	329	1,6	6
	Manual shaking	2,0	11	615	1,7	24
	Ultrasonicated	2,5	11	656	1,6	26
	AES (SAAF)	0	12	304	0	24
	AES (Wearcheck)	5	15	595	1	42
2175	No shaking	0,9	0,1	642	0,6	3,1
	Manual shaking	0,9	1,8	1 440	1,5	18
	Ultrasonicating	1,0	1,9	1 482	1,6	21
	AES (SAAF)	0	0,5	489	0	19
	AES (Wearcheck)	1	4	1 439	1	33

Sample preparation used by AES laboratories:

SAAF : Mechanical shaking mashine

Wearcheck : Ultrasonic bath

TABLE 13 : Analysis results of NBS standard reference material (SRM 1084 : Wear metals in lubricating oil)

Element	Concentrations ($\mu g\ g^{-1}$)	
	NBS	ICP
Al	98 ± 2	97,1 ± 1,7
Cr	100 ± 3	99,1 ± 1,3
Cu	98 ± 4	98,7 ± 1,3
Fe	100 ± 3	100,2 ± 0,6
Mg	98 ± 4	92,2 ± 1,4
Mo	97 ± 5	97,1 ± 0,6
Ni	101 ± 4	99,9 ± 1,7
Pb	101 ± 4	99,8 ± 1,7
Ti	99 ± 5	98,1 ± 1,4

SRM 1084 : Wear metals in lubricating oil.

NBS : Certified mean and estimated uncertainties constitute a simple summary of the range covered by 95 % confidence intervals computed separately for the data from each analytical method.

ICP : Mean and standard deviation of ten separate determinations using ICP-AES.

TABLE 14 : Analysis results of two Conostan C-21 working standards in xylene one year after preparation

	Concentrations ($\mu g\ cm^{-3}$)	
	1,00 $\mu g\ cm^{-3}$ standard	10,0 $\mu g\ cm^{-3}$ standard
Al	0,97	10,1
Cr	0,98	9,8
Cu	1,02	10,0
Fe	0,97	10,1
Pb	1,01	9,9
Si	1,04	10,2
Sn	0,99	9,8
Mg	0,12	9,5

TABLE 15 : Results of round robin sample (engine oil HQTS1) as reported in $\mu g\ g^{-1}$ by the various laboratories

Laboratory	Technique	Al	Cr	Cu	Fe	Pb	Si	Sn	Ca	Mg	P	Zn
Technikon Pretoria	ICP	7	4	28	33	14	16	4	2 786	144	994	1 120
Thabazimbi Mine	AAS	7	3	25	28	13	15	4	-	-	-	-
Vanderbijlpark Works	AAS	7	3	26	35	14	19	3	3 001	-	-	1 069
Pretoria Works	AAS	3	4	23	31	21	23	2	-	210	-	-
Newcastle Works	AAS	8	6	29	39	18	22	3	-	-	-	-
Sishen Mine	AAS	7	3	24	34	10	16	3	-	-	-	-
Ellisras Mine	AAS	8	5	25	31	12	15	-	-	-	-	-
Wearcheck	AES	9	7	24	38	13	15	2	4 902	187	907	985
SAAF	AES	9	3	22	33	22	17	3	-	146	-	380
Mean		7,2	4,2	25,1	33,6	15,2	17,6	3,0	3 563	172	950	1 058
Standard Deviation		1,8	1,5	2,3	3,5	4,1	3,1	0,8	-	32	-	68

- Not reported

TABLE 16 : Analytical results for the analysis of a series of oil samples by various laboratories (concentrations in $\mu g\ g^{-1}$)

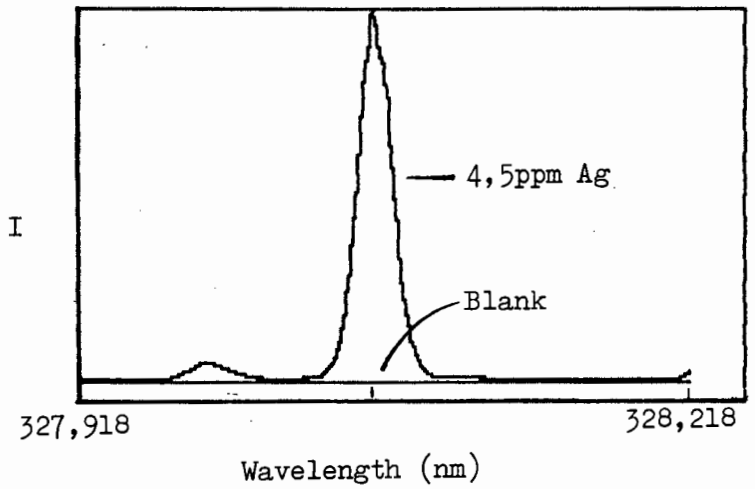
Sample number	Oil type	Al				Cr				Cu				Fe				Pb			
		AAS	AE1	AE2	ICP	AAS	AE1	AE2	ICP	AAS	AE1	AE2	ICP	AAS	AE1	AE2	ICP	AAS	AE1	AE2	ICP
2150	OHG140	0,5	0	-	1,7	<0,1	0,1	-	0,4	<0,1	0	-	1,1	9,0	73	-	91	9,5	2,3	-	4,7
2151	OHG140	0,5	0	-	2,2	<0,1	0,2	-	0,6	<0,1	0,3	-	1,0	20	92	-	112	32	24	-	39
2152	SAE30	15	40	16	15	<0,1	0	3	0,8	340	163	232	100	43	200	143	184	3	9	2	6,3
2153	OHG140	80	72	137	88	1,5	5,8	16	4,2	915	522	1664	1557	220	497	1146	1108	200	148	238	240
2155	OHG140	20	40	-	19	<0,1	0,7	-	1,3	1,0	4,9	-	3,3	205	400	-	426	9,0	17	-	11
2156	OHG140	3,5	0	-	3,6	0,5	0	-	0,6	2,5	5,4	-	8,1	28	118	-	195	1,5	0	-	2,0
2171	SAE90	1,5	0	5	2,5	<0,1.	0	2	1,2	8,0	12	15	11	270	304	595	656	1,0	0	1	1,6
2174	SAE140	1,5	0	-	1,1	<0,1	0	-	0,3	8,0	11	-	8,0	260	325	-	358	0,5	0	-	0,2
2175	SAE140	1,5	0	1	0,9	<0,1	0	0	1,0	0,5	0,5	4	1,9	390	489	1439	1482	0,1	0	1	1,6
2176	SAE140	1,0	0	-	0,9	<0,1	0,2	-	1,1	0,5	1,5	-	0,1	405	550	-	654	0,1	0	-	2,8
2177	SAE30	8,0	33	11	11	<0,1	0,2	8	2,0	2,5	11	3	3,6	34	79	39	39	7,0	6,2	3	8,6
2178	SAE10W	2,0	10	4	5,8	<0,1	0	5	1,1	5,0	17	8	5,7	4	17	2	5,6	2,0	0	0	3,0
2179	SAE30	9,5	21	9	7,7	<0,1	0	5	0,6	7,0	19	10	8,6	19	50	22	34	2,0	0	0	4,0

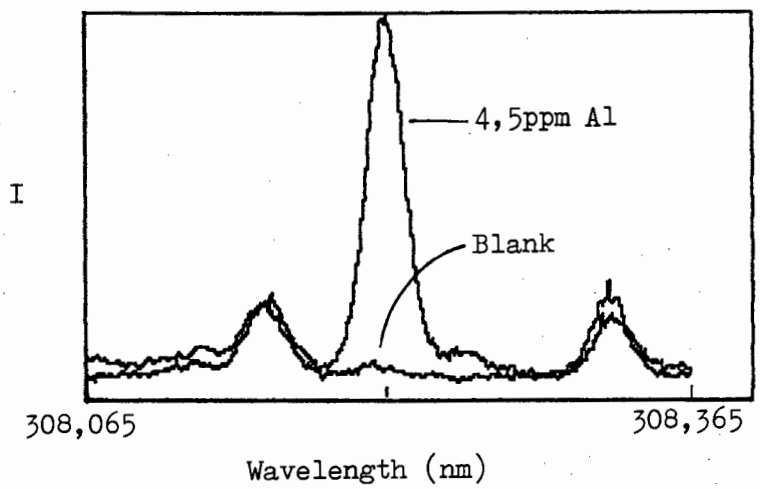
AAS : Atomic Absorption Spectrometry - ISCOR
AE1 : Atomic Emission with rotating disc electrode - SAAF
AE2 : Atomic Emission with rotating disc electrode - Wearcheck
ICP : Inductively coupled plasma
(-) not reported

TABLE 16 : (Continued)

Sample number	Oil type	Si				Sn				Ca			Mg			Zn			P	
		AAS	AE1	AE2	ICP	AAS	AE1	AE2	ICP	AE1	AE2	ICP	AE1	AE2	ICP	AE1	AE2	ICP	AE2	ICP
2150	OHG140	5,5	7,8	-	15	0,5	0	-	0,7	-	-	<1	<1	-	<1	2	-	5	-	880
2151	OHG140	3,0	0,6	-	3,1	<0,1	0	-	<0,1	-	-	5	<1	-	<1	3	-	7	-	836
2152	SAE30	15	31	8	45	7	13	5	8,8	-	3 256	2 692	370	521	417	>120	1 135	1 189	1 138	1 030
2153	OHG140	33	44	102	66	46	49	78	56	-	<100	36	14	<100	15	22	<100	43	613	692
2155	OHG140	120	174	-	122	0,5	0	-	1,5	-	-	1 667	377	-	407	>120	-	958	-	951
2156	OHG140	25	13	-	38	<0,1	0	-	0,4	-	-	35	11	-	17	4	-	9	-	892
2171	SAE90	12	24	42	26	<0,1	0	1	0,4	-	<100	169	32	<100	35	35	<100	69	549	552
2174	SAE140	15	17	-	8,7	<0,1	0	-	0,1	-	-	45	24	-	9	17	-	34	-	665
2175	SAE140	9,0	19	33	21	<0,1	0	2	0,3	-	<100	29	7	<100	6	13	<100	32	449	518
2176	SAE140	8,0	16	-	28	<0,1	0	-	0,5	-	-	16	7	-	3	13	-	17	-	664
2177	SAE30	6,5	24	6	9,0	3,0	0	1	1,4	-	3 830	2 958	442	556	493	>120	876	1 127	1 074	1 013
2178	SAE10W	4,0	13	1	9,1	2,5	0	1	0,4	-	3 014	2 717	383	101	93	>120	997	1 132	1 088	1 013
2179	SAE30	7,5	33	8	10	<0,1	0	1	1,7	-	3 041	2 544	168	527	451	>120	1 024	1 161	1 124	1 064

AAS : Atomic Absorption Spectrometry - ISCOR
AE1 : Atomic Emission with rotating disc electrode - SAAF
AE2 : Atomic Emission with rotating disc electrode - Wearcheck
ICP : Inductively coupled plasma
(-) not reported





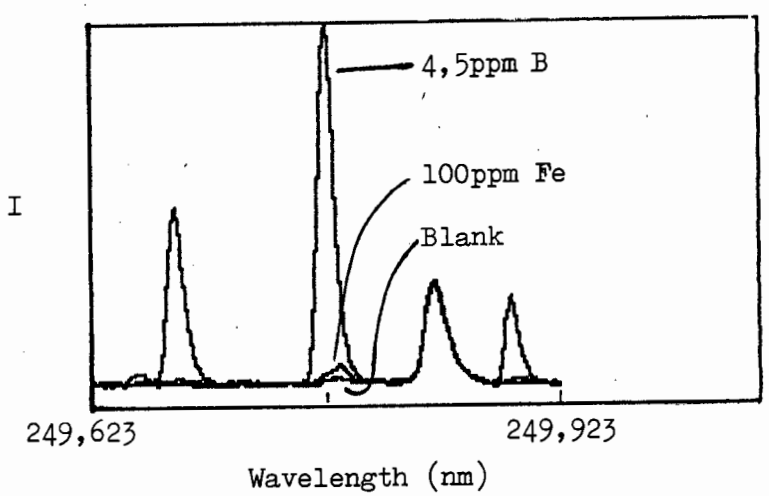


FIGURE 5 : Wavelength scans of the analysis lines for Ag, Al and B.

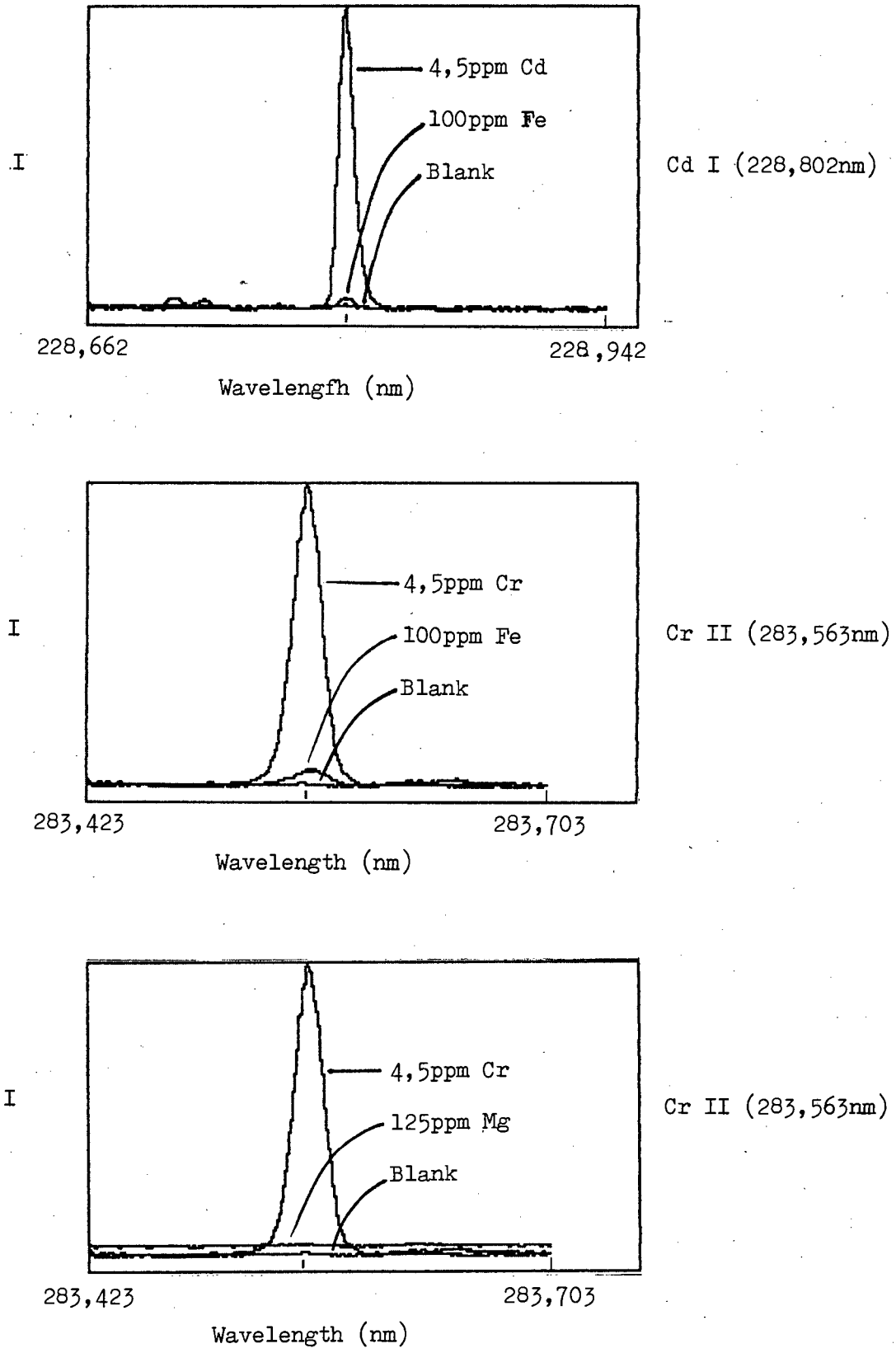
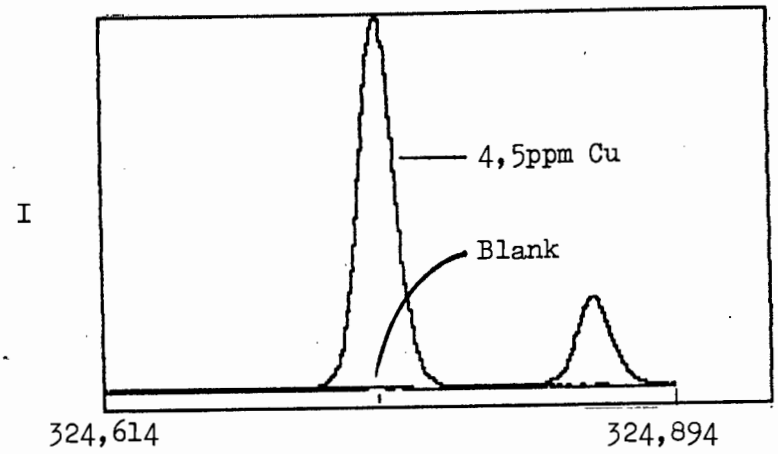
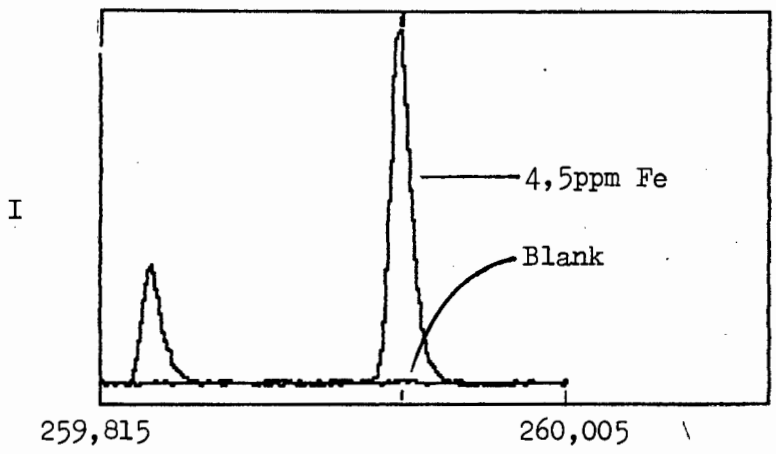


FIGURE 6 : Wavelength scans of the analysis lines for Cd and Cr.





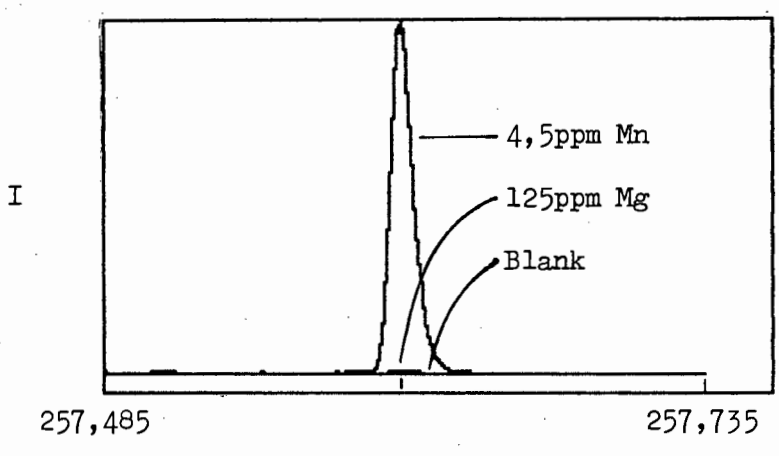


FIGURE 7 : Wavelength scans of the analysis lines for Cu , Fe and Mn.

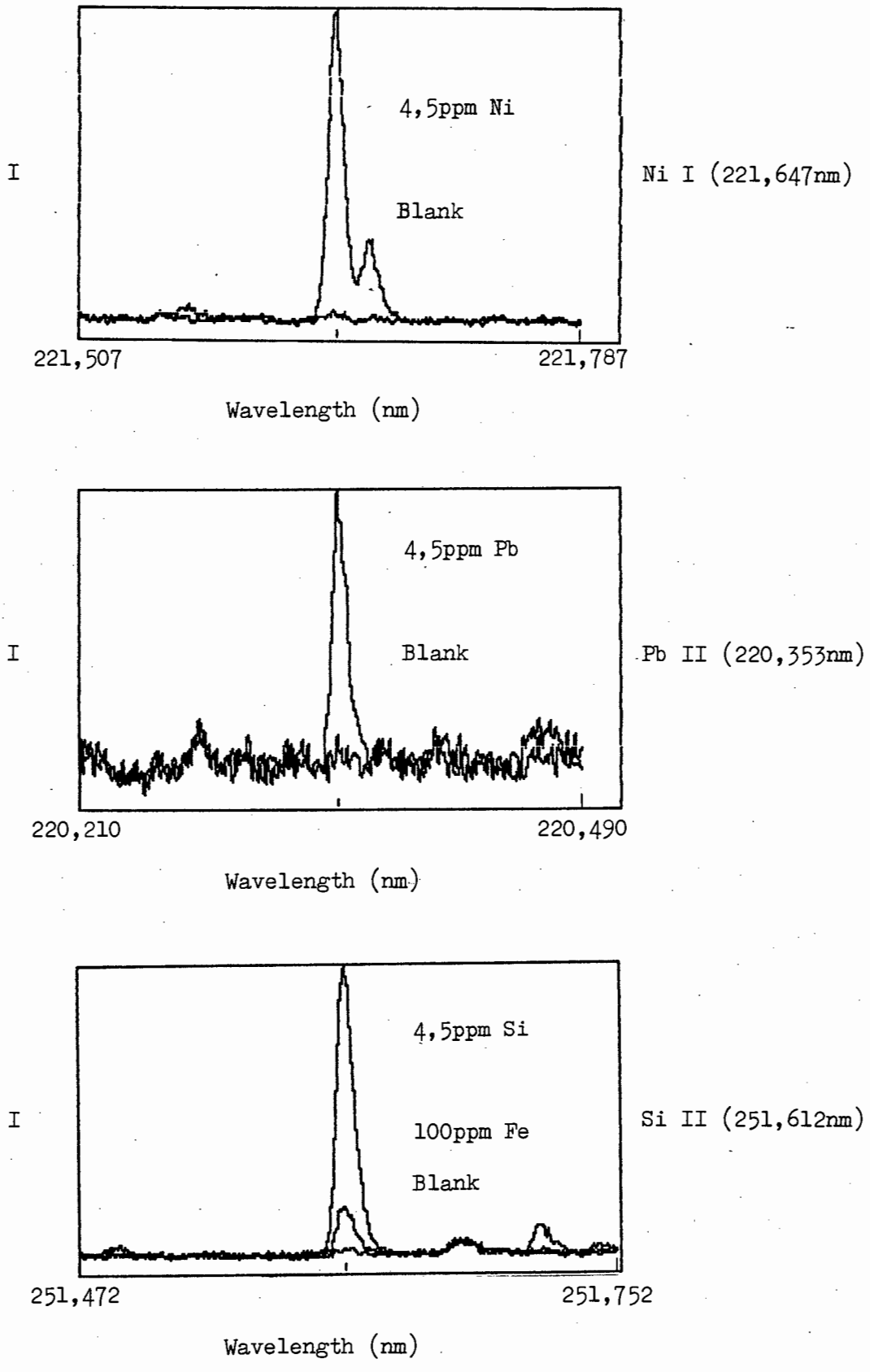
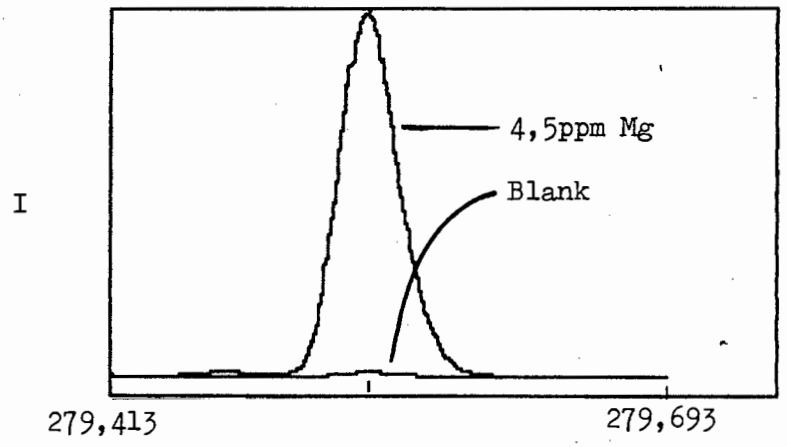
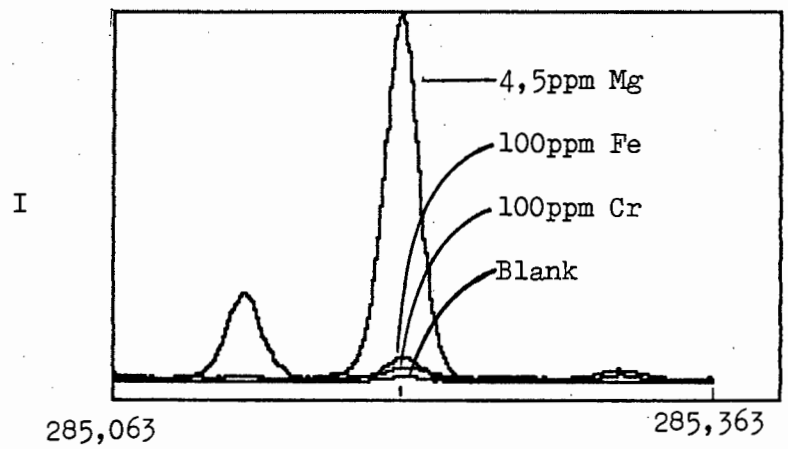


FIGURE 8 : Wavelength scans of the analysis lines for Ni , Pb and Si.





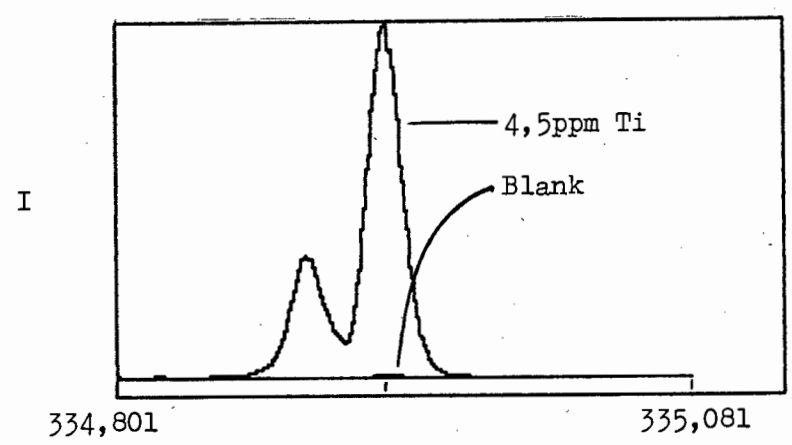


FIGURE 9 : Wavelength scans of the analysis lines for Mg and Ti.

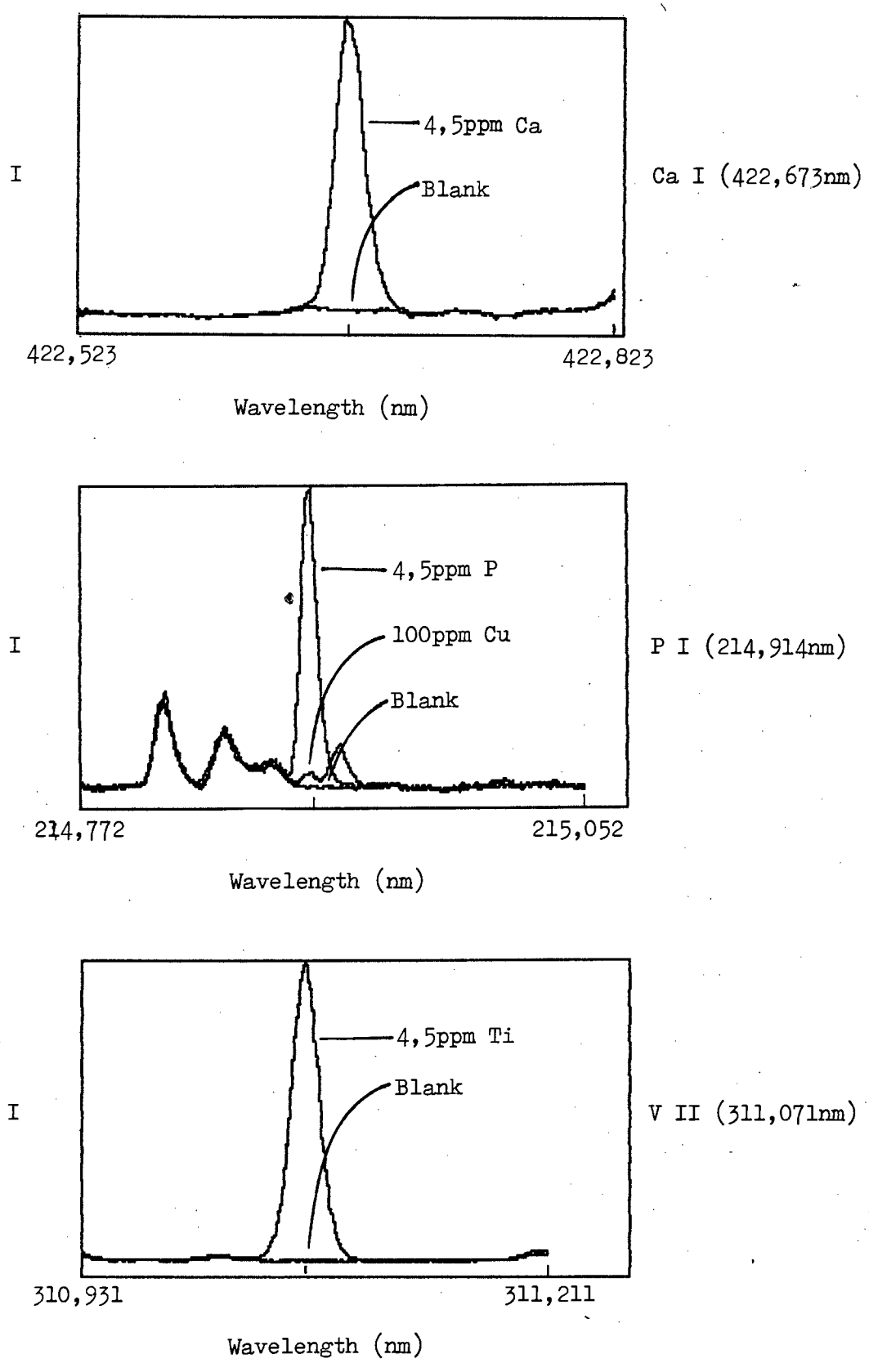


FIGURE 10 : Wavelength scans of the analysis lines for Ca , P and V.

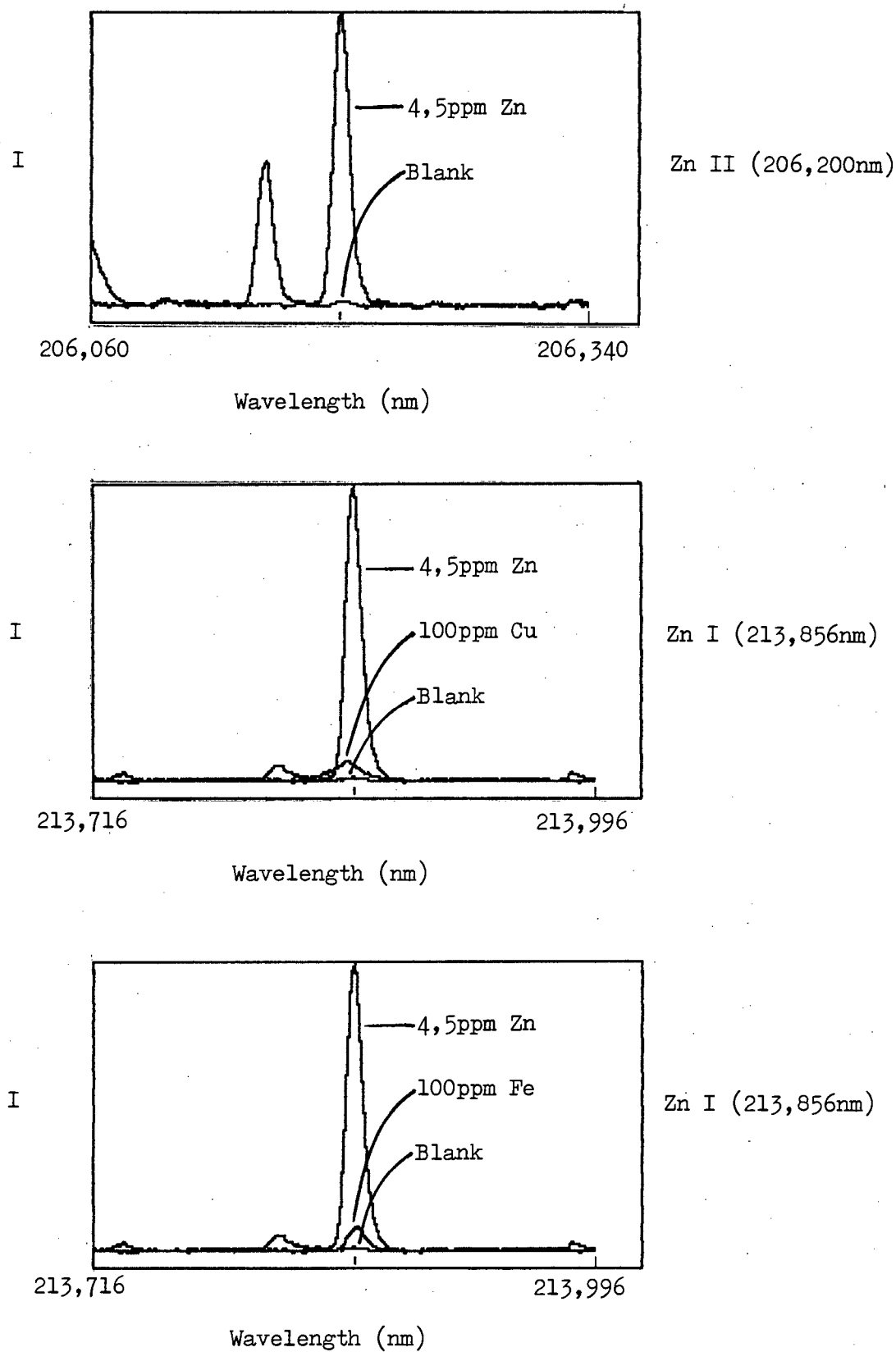


FIGURE 11 : Wavelength scans of the analysis lines for Zn.

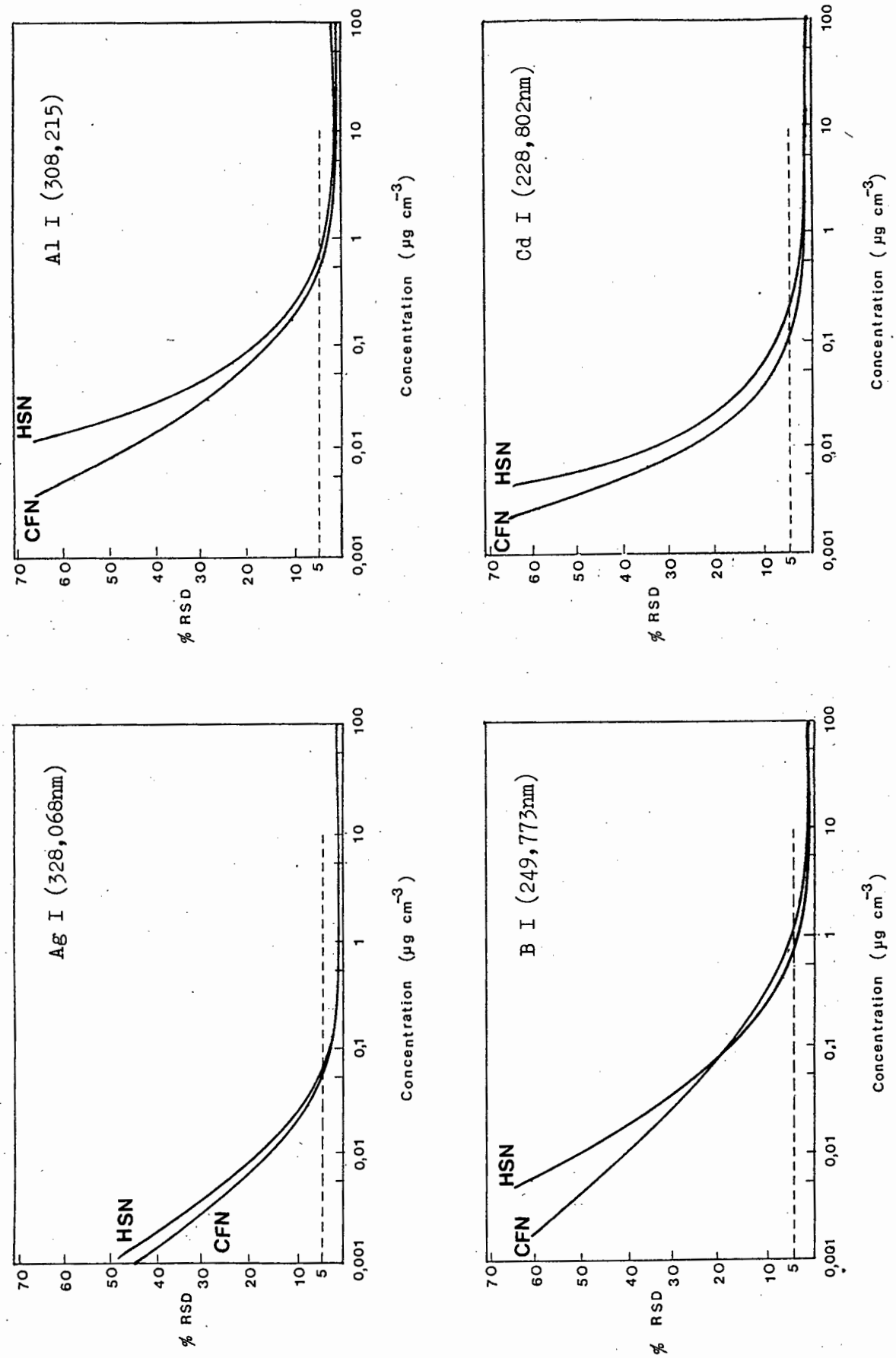
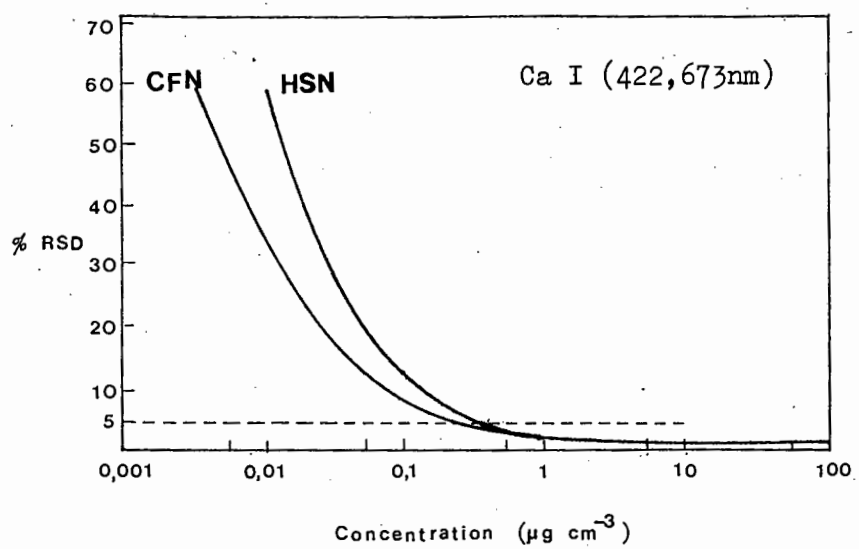
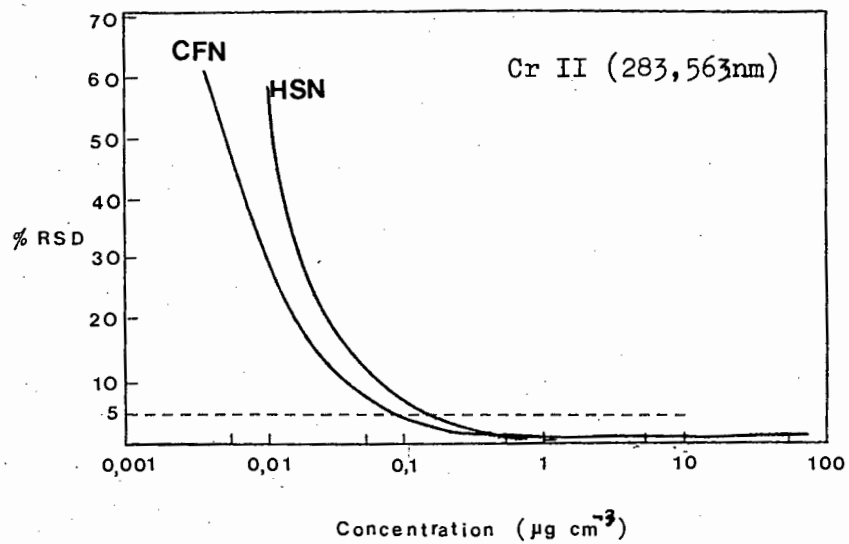
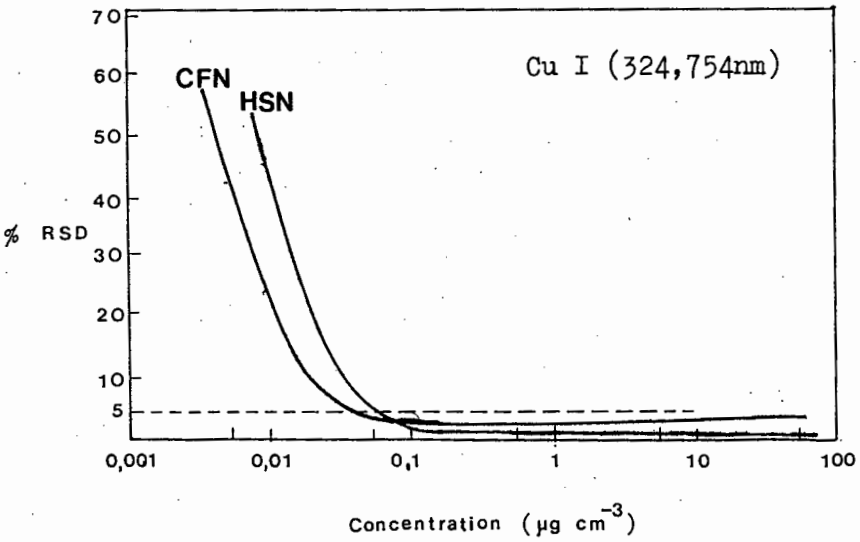


FIGURE 12 : Precision vs. concentration graphs for Ag, Al, B and Cd.







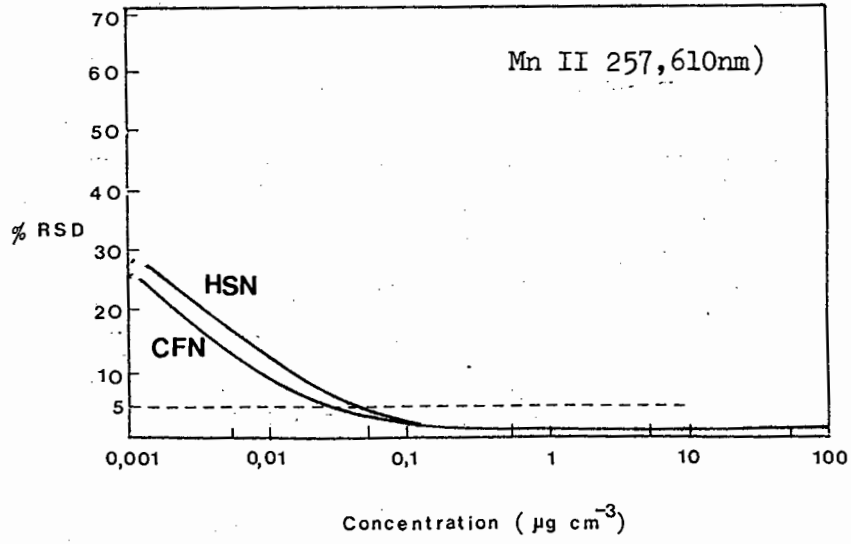


FIGURE 13 : Precision vs. concentration graphs for Ca, Cr, Cu and Mn.

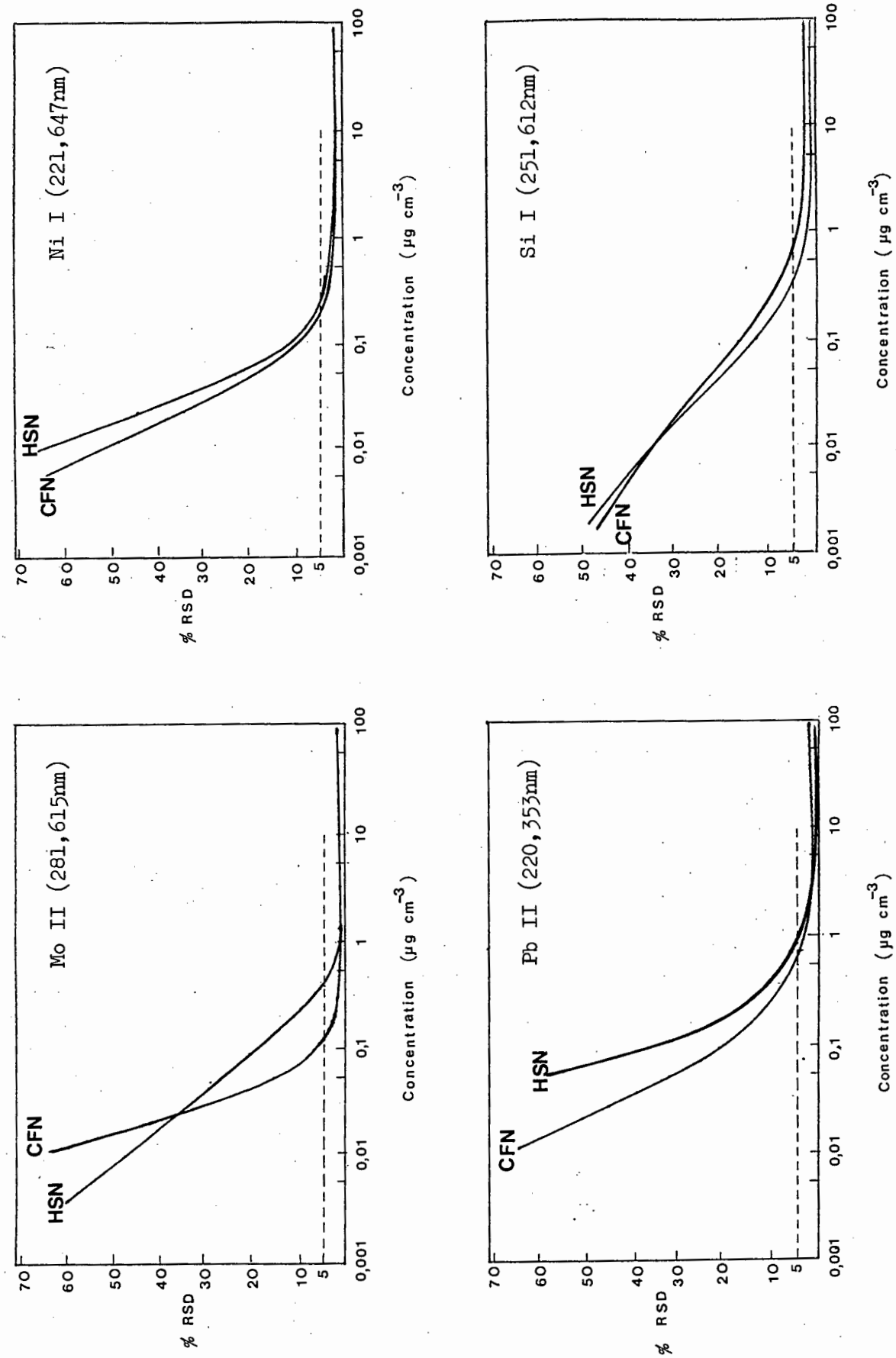
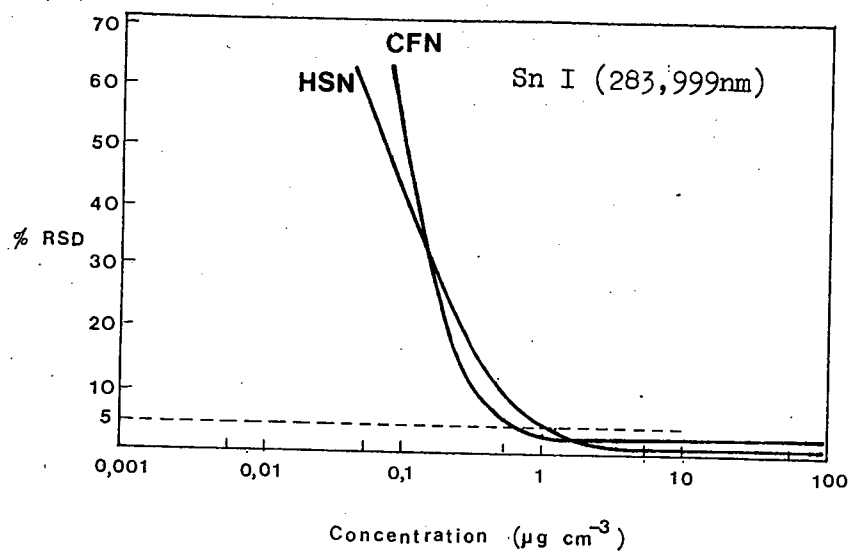
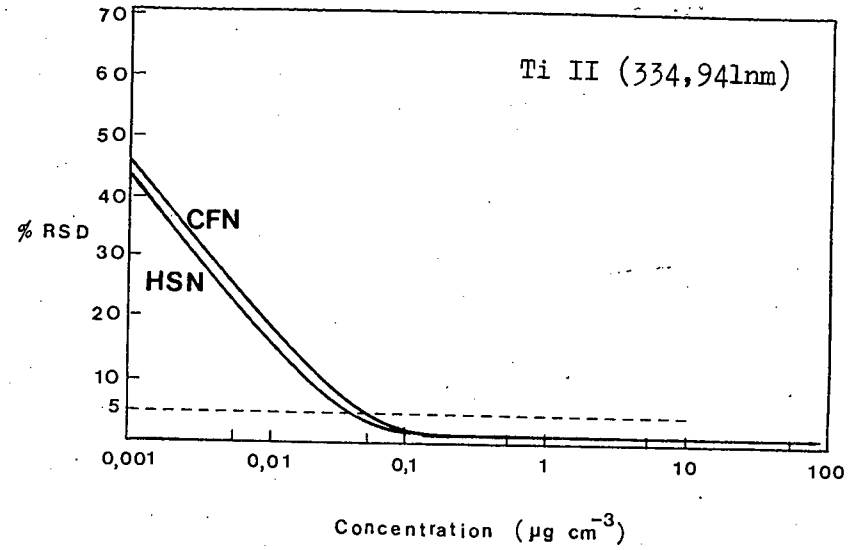
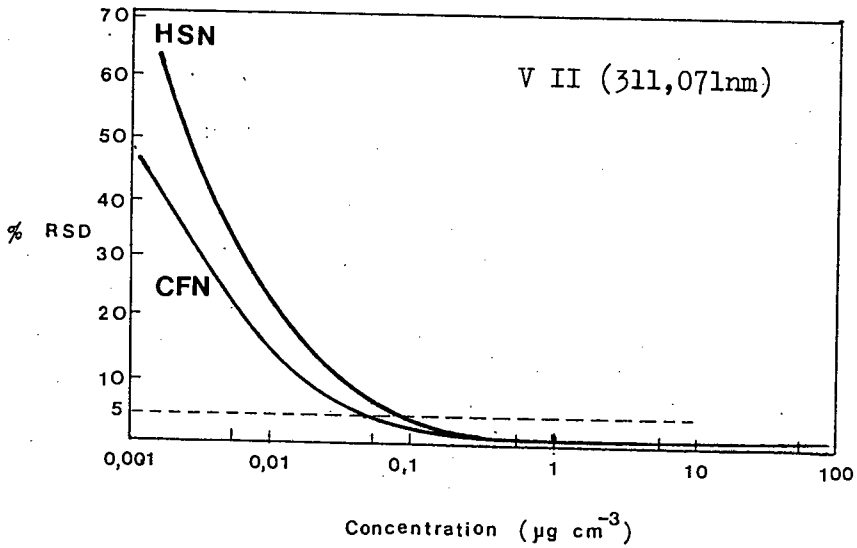


FIGURE 14 : Precision vs. concentration graphs for Mo, Ni, Pb and Si.







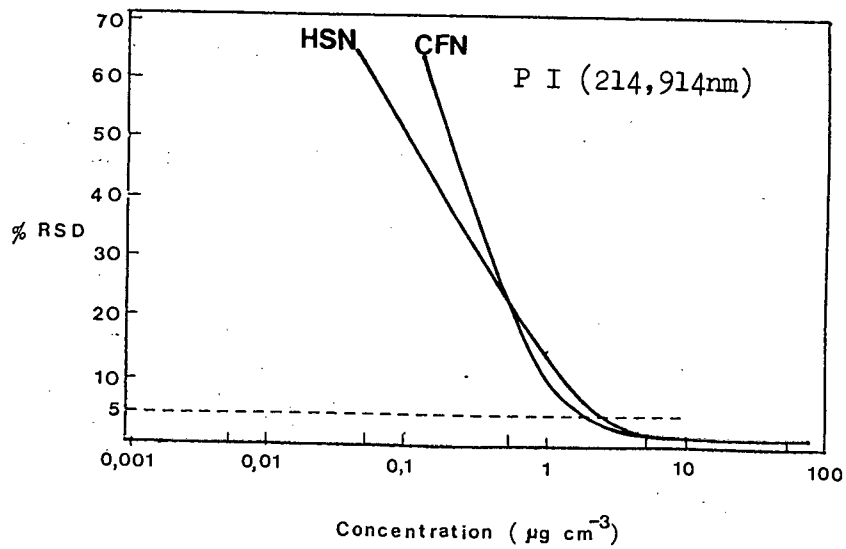
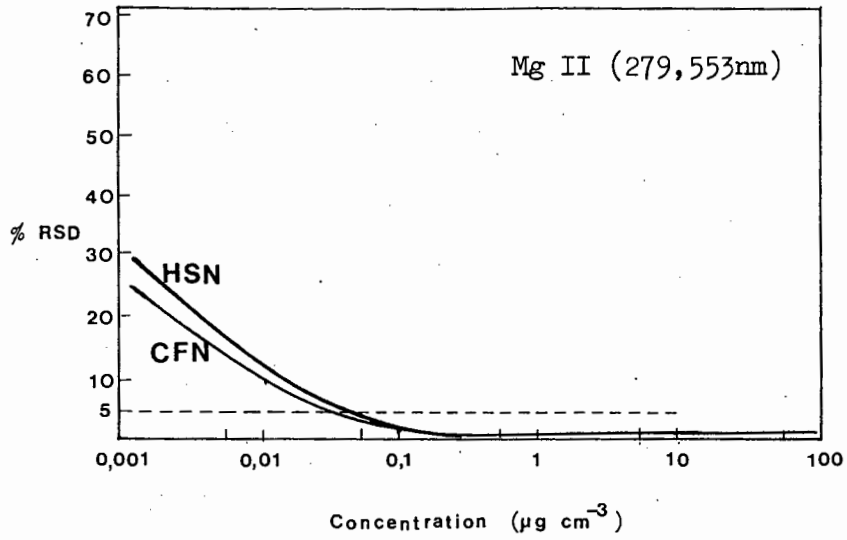
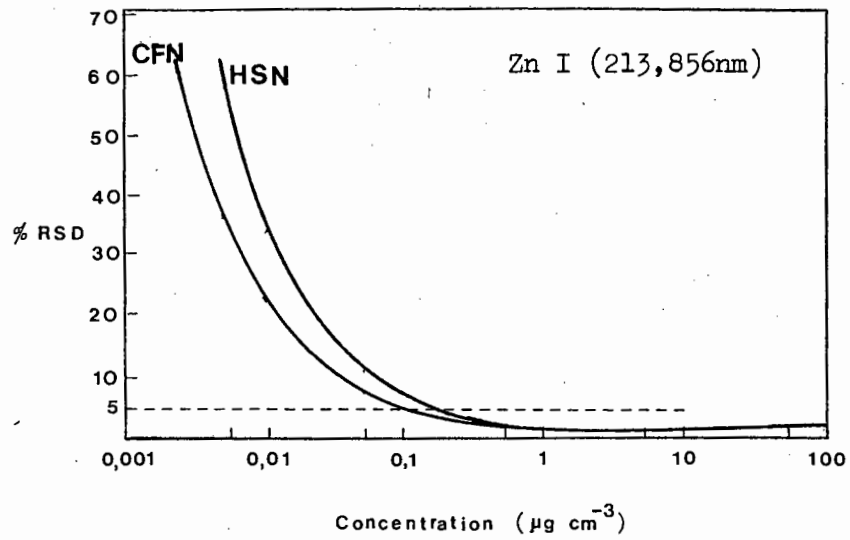
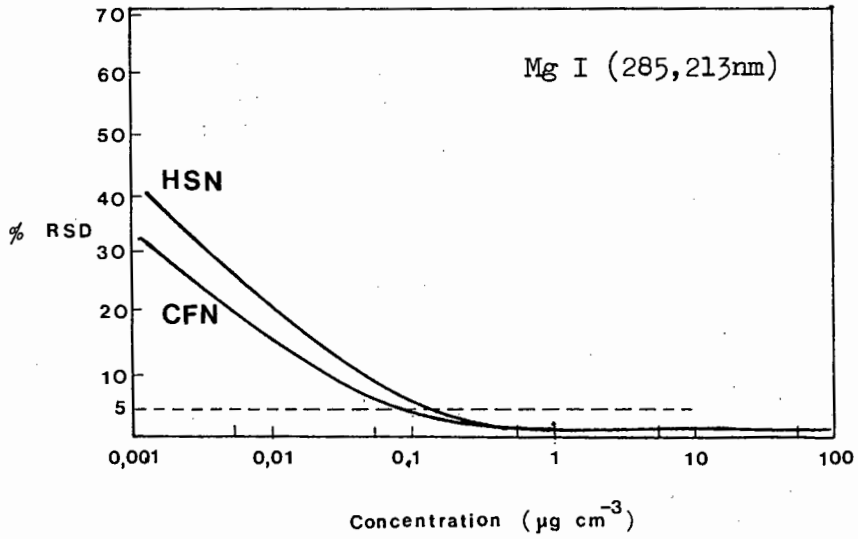


FIGURE 15 : Precision vs. concentration graphs for Sn, Ti, V and P.







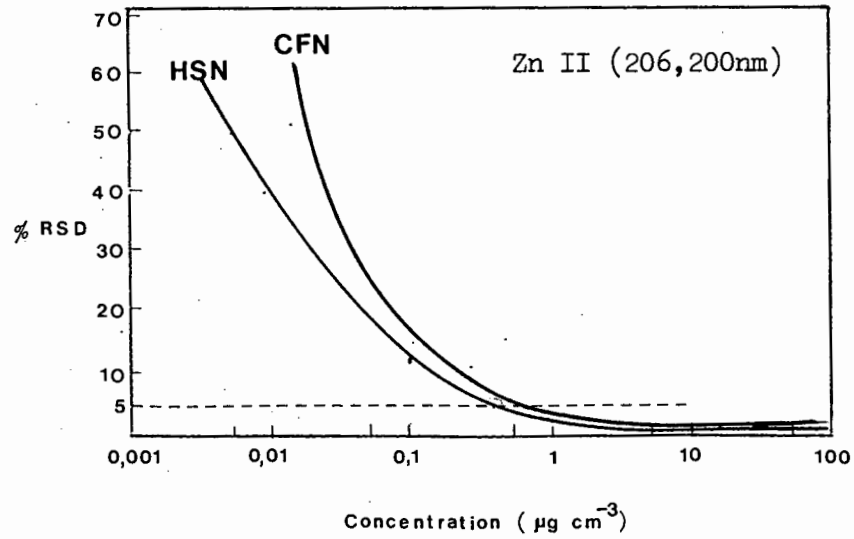


FIGURE 16 : Precision vs. concentration graphs for Mg and Zn.

APPENDIX I

RULES FOR THE SIMPLEX METHOD (From Moore, 1985)

Once the initial simplex has been established, the following rules and steps apply.

1. After each single response measurement, a move is made.

In the interests of speed, replicate measurements are not normally made. The method is designed so that any false high responses generated are eliminated.

2. The simplex moves by rejection of the point that shows the worst response and replacement of that point with its mirror image across the hyperface of the remaining four points.

If the vertices of the four-dimensional simplex are represented by the coordinate vectors S1, S2, S3, S4 and S5, where S5 has the worst response, then elimination of the most undesirable response leaves the hyperface S1, S2, S3 and S4 with centroid C, where

$$C = (S1 + S2 + S3 + S4)/4 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

The new simplex is defined by this hyperface, and a new vertex S6 is generated by the reflection of S5 across the hyperface through C:

$$S6 = C + (C - S5). \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

If the new vertex yields the worst response in the new simplex, the application of Rule 2 would result in the reflection of the simplex back to the previous simplex, and it would become standard. Hence, Rule 3 is needed.

3. **If the new vertex shows the worst response in the new simplex, the vertex associated with the second-worst response is rejected, and the moves continue.**

4. **If a vertex has not been replaced in 5 simplices before Rule 2 was applied, the response at the persistent vertex must be retested.**

This rule is necessary so that the simplex will be prevented from circling a possible false high response.

The simplex may start to move beyond the permitted hyperspace by exceeding one or more of the four plasma variables (i.e. a boundary violation). A new vertex may call for an observation height lower than the top of the quartz torch or a power higher than can be supplied by the generator. In such an event, Rule 5 is applied.

5. **If the new vertex lies beyond the boundaries of the interdependent variables, the response must not be observed but a very undesirable response must be assigned to that vertex.**

The application of Rules 2 and 3 will then result in the simplex returning to a position inside the boundary limits.

The identification of a situation in which a limitation on a variable prevents the attainment of a better response is one of the beneficial practical results of the simplex method of optimization.

Once an optimum has been found, the rules force the simplex to circle around the optimum region. The smaller the simplex at this stage, the more accurately the optimum can be defined. Once the simplex shrinks to such a size that the indeterminate errors involved in the response measurement mask the true differences between the vertex responses, the simplex will wander erratically near the optimum.

The **modified simplex procedure** employs the Rules for the basic simplex, but also allows for the contraction or expansion of the simplex to enable it to travel faster over the response surface and to define the final optimum more precisely. The operations of expansion and contraction are added to the operation of reflection.

If an initial simplex has the responses R1, R2, R3, R4, R5 in descending order, the following procedure must be followed.

For any particular parameter,

V_w represents the value of the parameter associated with the worst response, R5.

The new parameter V_R will then be defined by the equation:

$$V_R = C + Z(C - V_W), \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

where the centroid C is given by:

$$C = (V_1 + V_2 + V_3 + V_4)/4, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

and the expansion coefficient Z is taken as 1. V is the value of a parameter associated with a particular response.

If the response at the new vertex is greater than R1, expansion of the simplex may be justified, and new parameters are calculated by the use of equation (3) when Z = 2. If the response at this expanded vertex is better than at the reflected vertex, the expanded vertex is used to define the new simplex. If the response is worse, the original reflected vertex is used.

If the response at the new vertex is less than R1 but greater than R3, the reflected vertex (Z = 1) is used to define the new simplex, i.e. no expansion or contraction is attempted.

If the response at the new vertex is less than R3 but greater than R5, a positive contraction is attempted, and new parameters are calculated by the use of equation (3) when Z = +0,5. If the response at the contracted vertex is better than at the reflected vertex, the contracted vertex is retained in the new simplex. If the response is worse, the original reflected vertex is retained.

If the response at the new vertex is less than R5, a negative contraction is applied, and the new parameters are calculated by the use of equation (3) when Z = -0,5. Irrespective of the success or failure of this negative contraction, the contracted vertex is retained in the new simplex but, in the latter event (failed negative contraction), the second-worst response is rejected on the next simplex cycle. As in the case of a boundary violation, this causes the simplex to change to a direction that may be more favourable.

When the differences in response or step sizes of the plasma parameters become smaller than a certain value, the simplex can be stopped.

APPENDIX II

DESCRIPTION OF APPARATUS

1. Plasma source.

   Torch: quartz with continuously variable argon flows for the outer, intermediate and sample carrier gas.

   Nebulizer: 1. corrosion-resistant, cross-flow pneumatic
   2. high-solids, Babington type

   RF-Generator: 2500 watts maximum at 27,12 MHz with crystal controlled frequency and automatic power control.

2. Monochromator.

   Optics: crossed Czerney-Turner, 750 mm

   Wavelength range: 178-535 nm

   Grating: 2400 lines mm^{-1}

   Slew rate: 2000 nm s^{-1}

   Linear dispersion: 0,25 nm mm^{-1} from 178-265 nm
   0,50 nm mm^{-1} from 265-535 mm.

   Temperature control: 35°C ± 0,05

   Purge option: nitrogen, continuous flow to allow determination of elements in the low UV region.

3. Data acquisition system.

   Computer: 64 K Apple IIe microcomputer, dual mini-floppy discs, high resolution graphics video monitor and Apple dot matrix printer.

   Software: Highly user interactive, menu-selectable software modules written in BASIC providing scanning, single and multi-element analysis, line library, standardization and data gathering, graphic display and report writing.

4. Readout system.

Detectors: 2 photomultipliers (R427 for the range 178-265 nm and R300 for the range 265-535 nm)

Range: 0 to 10 volts; 0 to 4095 counts

Integration time: 0,4 s minimum, analytical
0,03 s minimum, scanning.

5. Sample feed.

A Rainin Rabbit peristaltic pump was used to feed the sample to the nebulizer at a constant rate. "Isoversinic" flow tubes (Gilsón Medical Electronics, France) with inside diameters of 1,0 and 2,0 mm were used for the cross-flow and high solids nebulizers respectively. With these flow tubes the flow could be varied between 0 and 7,3 cm^3 min^{-1}.

APPENDIX III

REAGENTS AND STANDARDS

1. Chemicals and stock solutions used

The following chemicals were used for the preparation of stock solutions and intermediate standards:

- Conostan C-21 "oil based organometallic standard solution for the determination of metals in lubricating oil". (Conostan Division of the Continental Oil Company, Ponca City, Oklahoma, USA.) containing 900 $\mu g\ g^{-1}$ each of 21 different elements (Ag, Al, B, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, P, Pb, Si, Sn, Ti, V and Zn).
- Conostan individual oil based organometallic standard solutions for the determination of additives in lubricating oil: each containing 5000 $\mu g\ g^{-1}$ of metal concerned (i.e. Ca, Mg, P and Zn).
- Conostan stabilizer liquid for use in Conostan organometallic lubricating oil standards.
- "Metal-free" oil: Shell Vitrea oil no 100 (Shell Chemicals) was used to prepare the blank solution.
- Xylene: Chemically pure grade (Holpro Analytics (Pty) Ltd) for use as solvent for all standards and samples.

2. Preparation of intermediate standards

Intermediate standards were prepared by weight in polypropylene containers, using a three decimal place balance. Oil and standard solutions were transferred to the containers by means of disposable syringes to avoid contamination.

- 10,0 and 100 $\mu g\ g^{-1}$ 21 elements in oil : 1,111 and 11,111 g of the Conostan C-21 standard was placed in two separate polypropylene containers to which 1,00 g of the stabilizer liquid was added. Metal-free oil was then added to each to make up the mass to 100,00 g.
- 0,500 $\mu g\ g^{-1}$ of 21 elements in oil : 4,500 g of the 10,0 $\mu g\ g^{-1}$ standard was placed in a polypropylene container to which 1,00 g of the stablizer liquid was added. Metal-free oil was then added to make up the mass to 100,00 g.

- 2500 µg g^{-1} Ca and Mg : 30,00 g of each of the respective Conostan organometallic standard solutions were mixed in a polypropylene container.
- 2500 µg g^{-1} P and Z : 30,00 g of each of the respective Conostan organometallic standard solutions were mixed in a polypropylene container.

APPENDIX IV

LIST OF ABBREVIATIONS AND SYMBOLS

Abbreviations

AAS	:	Atomic absorption spectrometry
AES	:	Atomic emission spectrometry
BLK	:	Blank solution (10% (m/v) metal-free oil in xylene)
DCP	:	Direct current plasma
ICP	:	Inductively coupled plasma
ICP-AES	:	Inductively coupled plasma-atomic emission spectrometry
IEC	:	Inter element correction
ISCOR	:	South African Iron and Steel Industrial Corporation
MIBK	:	4 Methyl-pentan-2-one or Methyl isobutyl ketone
NBS	:	National Bureau of Standards
ppm	:	Parts per million ($\mu g\ g^{-1}$ or $\mu g\ cm^{-3}$)
RDE	:	Rotating disc electrode
SAAF	:	South African Air Force
SASOL	:	South African Coal, Oil and Gas Corporation
SATS	:	South African Transport Services
SBR	:	Net signal-to-background ratio
SOAP	:	Spectrometric Oil Analysis Programme
SRM	:	Standard reference material
Std	:	Standard (4,5 $\mu g\ cm^{-3}$ composite oil in xylene standard)

Symbols

c	:	Concentration (in $\mu g\ g^{-1}$, $ng\ g^{-1}$ or $\mu g\ cm^{-3}$)
c_D	:	Limit of determination (in concentration units)
c_L	:	Detection limit (in concentration units)

F	:	Frequency of routine analytical usage
I	:	Relative intensity
I_b	:	Intensity of the blank
I_n	:	Net analyte intensity
m	:	Analytical sensitivity or the slope of the calibration curve
P	:	Plasma parameter
P_u	:	Compromise optimum parameter
s_B	:	Standard deviation of the blank
W	:	Weighting factor

ACKNOWLEDGEMENTS

I wish to thank all those people who have assisted me during this research:

My supervisor, Prof MJ Orren, for his valuable help and advice.

The Research Committee of Technikon Pretoria for financial assistance.

Dr WHJ de Beer and the personnel of the School of Chemical Sciences (Technikon Pretoria) for their support and permission to use their laboratories and equipment.

Mr Nick Sidiropoulos (ISCOR) for providing the oil samples and for organising the round robin analyses.

The SAAF oil laboratory for providing the emission spectrometric analyses.

Mrs Lesley Crawford (Wearcheck (Pty) Ltd) for analysing some of the samples and her valuable advice.

Mr Glynn Moore (Mintek) for his help with the simplex optimization.

Mrs Jenny Seager for typing this thesis.

Last, but not least, to my wife, Fiona, and my sons, Michael, Stephen, Pieter-Julian and Chrisjan, for their patience and moral support.